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Journal

VOLUME 19, NUMBER 6

DECEMBER 1958

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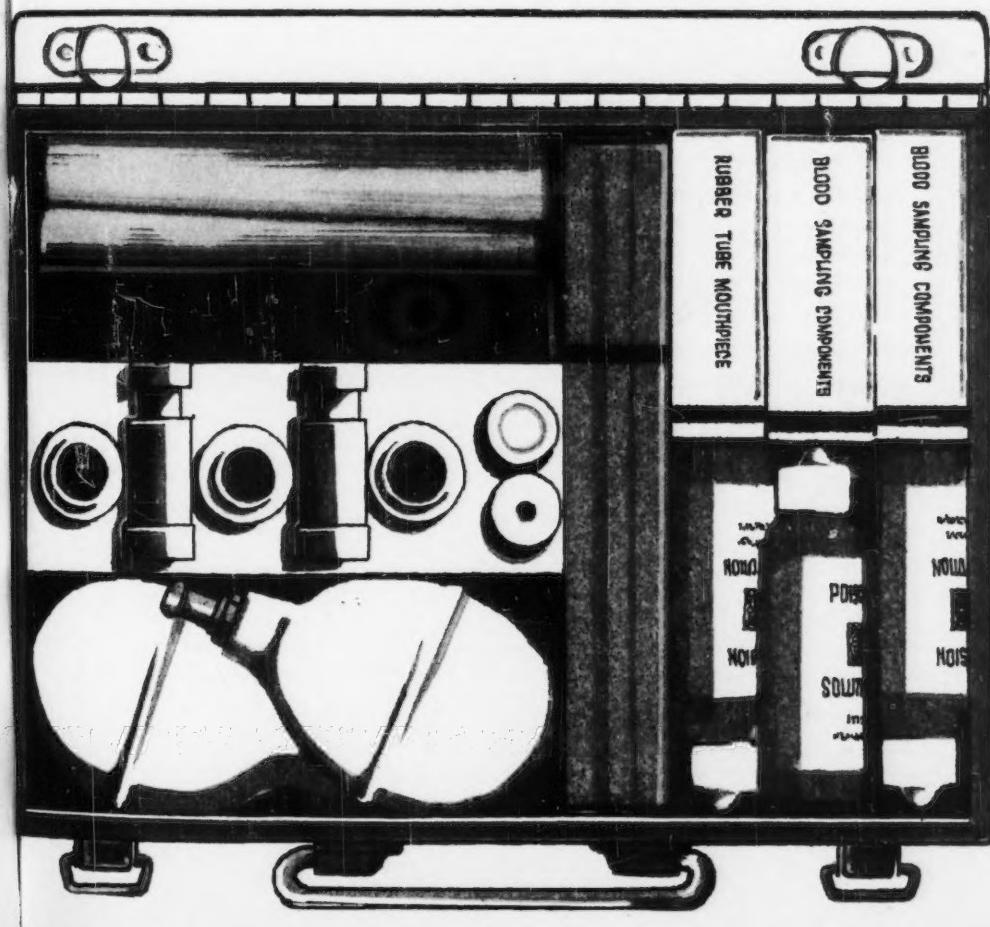
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President's Page



Admiral H. G. Rickover, USN, gave a commencement address last June at the Stevens Institute of Technology. A cogent paragraph from the address has been quoted elsewhere but it is well worth repeating again and again.

"The intellectual content of a profession, the field of knowledge it monopolizes, must of course be mastered before a man may begin to call himself a professional person. But it is not something learned once and for all in a prescribed course of study. Knowledge increases and a man must keep up with it, so he is never done with learning. In fact, he himself is obligated to carry forward the knowledge on which his profession is based and to ensure that it is handed down to new members. In a very intimate sense, his own specialty is a professional man's personal concern and responsibility. Its continued advance can be brought about only by the efforts of present members of the profession who themselves are indebted to the contributions of past members. A professional man who cannot make original contributions to his field of knowledge can at least enhance the prestige or standards of his profession. Above all, he can and must support the institutions which train future colleagues."

A handwritten signature in cursive script that reads "Kenneth W. Nelson". The signature is fluid and written in black ink on a white background.

AMERICAN
Industrial Hygiene
ASSOCIATION *Journal*

Volume 19

DECEMBER 1958

Number 6

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Alice Hamilton, M.D.

May R. Mayers, M.D.

Through this brief article we of the American Industrial Hygiene Association wish to recognize and do honor to Dr. Alice Hamilton on the occasion of her ninetieth birthday which she will celebrate in February, 1959. It seems most appropriate that this tribute has been authored by Dr. May R. Mayers, also a woman, a physician, and a person of considerable esteem in industrial hygiene. Ed.

IT IS A major achievement to arrive at the age of ninety as hale and hearty as is Dr. Alice Hamilton to-day, and as vitally interested in everything that is going on in the world. It is also a major achievement to be so deeply loved and admired by all of her many friends and professional colleagues. But major achievements are what we have come to expect from Alice Hamilton and we accept them as an inseparable part of her colorful life.

As a pioneer in the field of industrial hygiene she has become a glowing symbol of our fondest aspirations, many of which owe their early beginnings to her crusading zeal, her vision, and her distinguished scientific achievements. As a pathfinder and educator, she has provided us with many guide posts to illuminate our road, and these have helped to give direction to the evolution of this relatively new branch of public health—one which is still in its infancy, but which is now dramatically riding the wave of the future. Much has been written about these pioneering efforts. And the readers of the Journal are entirely familiar with her technical publications. *Industrial Poisons in the United States* published in 1929, *Industrial Toxicology* first published in 1934, and revised¹ in 1949 in collaboration with Dr. Harriet Hardy, are classics in our field. This work need not, therefore, be recapitulated here.

Of great interest, however, in connection with Dr. Hamilton's writings is the fact that early in her career, as a student of pathology and anatomy under Dr. Simon Flexner, she learned what she has since characterized as "that important part of research, the thorough and critical review of all that has been written on one's

problems and the scrupulous care one must use to give credit where credit is due." This is reflected in all of Dr. Hamilton's technical books and papers which are conspicuous for their meticulous documentation, their thorough and critical review of the literature, their perspective and balance. Dr. Hamilton was most fortunate both in this country and abroad in having had the opportunity to study under leading medical scholars: Simon Flexner, William Osler, W. J. Howell, William Welch, and others of similar stature. In her modest autobiography *Exploring the Dangerous Trades* is revealed a woman of original mind and warm personality capable of creating as well as profiting fully by her exceptional opportunities. It is a fascinating story, delightfully written. Everyone should read it.

For Alice Hamilton, industrial hygiene has always been only one part of the larger field of medicine, particularly that of public health, and of the larger world in which she lived—one in which poverty, slum housing, inequality of opportunity, inadequate nutrition, inadequate medical care and two world wars provided a distressing and frustrating back-drop. She was very close to all of these problems as a result of her long residence at Hull House, in Chicago, where Jane Addams was the magnet to which independent, high-minded men and women, idealists from all over the world, foregathered to see what could be done to mitigate the inequities in the social fabric of their time. To the problems in this area, where fuzzy thinking is all too common, Dr. Hamilton brought to bear a disciplined scientific mind of high intelligence, and a liberalism which was immune to extreme ideologies either of the right or the left. And from her intimate contact with these social problems and the great personalities of her day, with whom she joined in seeking solutions, she was enabled to bring to medicine—and particularly to the field of industrial hygiene—a broad vision of future goals and possibilities, many of which are only now beginning to unfold.

It must be heartwarming to Alice Hamilton to see the field of industrial hygiene expanding beyond the prevention of health hazards in industry to include all occupations and all aspects

of occupational health; to see the growing interest in plant medical services and medical care directed toward the prevention of disease and the promotion of optimum health and well being. It must be gratifying to her, also, to see the many professional disciplines which are now cooperating in a common effort toward these goals—engineers, chemists, physicists, physiologists, statisticians, psychologists, nurses, nutritionists, as well as many specialized branches of medicine; to see the extent to which the laboratory is contributing not only to a quantitative evaluation of occupational exposures in terms of safe dosage, but to the early detection and correct diagnosis of the occupational diseases; to see the extent to which management, government and labor are working with these technical groups to translate their data into practical realities. And yet she knows, perhaps better than any of us, how long is the road we still have to travel.

Of Scotch-Irish, mid-western, pioneer ancestry, Alice Hamilton was born in New York City in February 1869 when her mother, an Eastern woman, was there on a trip. From the age of six weeks she grew up in the old family home in Fort Wayne, Indiana. There, with three sisters very nearly her own age, a much younger brother, and eleven cousins, she spent a happy childhood in a highly cultivated and intellectual atmosphere. Since neither her mother nor her father believed in formal schooling, the children were taught at home. She says, "The religion we were taught was sober.—The Bible was more familiar to us than any other book." While the subject matter studied was apparently short on mathematics and science, they were thoroughly grounded in what their parents thought important: languages, literature, and history. One wonders whether "the labor of searching for the knowledge we wanted" was not responsible for Dr. Hamilton's original and unfettered mind and the high standards of scholarship which may be seen in all of her work.

From Mrs. Porter's genteel boarding school in Farmington, Conn., Alice Hamilton entered medical school at the University of Michigan at the age of twenty-one. She tells us that she selected medicine as a career so she could "Go anywhere I pleased to far off lands or to city slums—and be quite sure I could be of use anywhere..." Her sense of social service was thus apparent at an early age.

On receiving her M.D. she went to Germany where she did graduate work in bacteriology and pathology under leading scholars in Leipzig and Munich from 1895-6 under conditions which

were intellectually challenging and socially delightful. From 1896-7 she worked under some of our foremost scholars at Johns Hopkins. There followed work at the University of Chicago, and internship at the New England Hospital for Women in Boston, a professorship in pathology at the Women's Medical School of Northwestern University in Chicago and work at the Memorial Institute for Infectious Diseases. These years were devoted to research in bacteriology and pathology and to teaching. She was not interested in going into the practice of medicine, though she started a baby clinic at Hull House when the need seemed urgent.

It was the publication of Thomas Oliver's *Dangerous Trades* which first opened her eyes to the existence of industrial health hazards. And as she looked about her, she found them among the people with whom she lived and worked—her own neighbors at Hull House. In 1910 she was appointed chief investigator for the Illinois State Commission to Study Industrial Diseases, the first of its kind. And with her characteristic sense of humor, Dr. Hamilton comments on the "ignorant optimism" revealed by the survey. She was now embarked upon her distinguished career, a branch of medicine which gave scope to both her great sense of social responsibility and her deep interest in the medical sciences.

The following summer she was sent to attend the International Congress on Occupational Diseases in Brussels. And so, at a time when industrial hygiene, as we now know it, was practically non-existent in this country, she began to study the methods used for the control of industrial health hazards in the older industrial countries, particularly England and Germany, where these problems had been receiving a great deal of serious attention for some time past. When in 1911, she began her work as investigator for the Bureau of Labor Statistics of the newly formed U. S. Department of Labor, she was able to bring to this country her experience from abroad. Her pioneer studies of the "Dangerous Trades" in the United States, which included the war industries during World War I, covered a broad field with which we are all familiar. Her last such study was in 1937 when she investigated the problems of carbon disulphide poisoning in the manufacture of viscose rayon, then a new industry. Climbing ladders and walking slippery planks in workrooms, sometimes full of noxious air contaminants, seemed an incredible activity for a young woman of Alice Hamilton's genteel background. It startled many an employer. She visited not only workshops but

workers' homes. Her clinical and sociological observations were always very astute. To her, the work was a social and a medical challenge, a fascinating adventure. It was highly picturesque.

In none of her field studies for the U. S. Department of Labor, which took her back and forth across the country many times, did she have any legal authority to enter plants. Nor did she have legal powers of enforcement. Against seemingly insuperable obstacles, however, she got things done by sheer force of personality and tireless dedication to her cause. And the ball which she started rolling has been gaining momentum ever since. She is very modest in recording how, in time, she was called into consultation with increasing frequency by industrialists and others to assist in the solution of industrial hygiene problems—problems which might still have gone unnoticed—had she not persevered in spreading enlightenment wherever she went. Years later she revisited many of these plants and was gratified to see the strides that had been made.

During these years she continued to regard Hull House as her home and went back there whenever she could. She says, "To me, the life there satisfied every longing for companionship, for the excitement of new experiences, for constant intellectual stimulation, and for the sense of being caught up in a big movement which enlisted my enthusiastic loyalty." Those of us who grew up before World War I, can readily understand her devotion to Hull House. For, at that time, we believed with Alice Hamilton that the world was getting steadily better; that all one had to do was to lend a helping hand; and that the Settlement House was the place to begin. The first World War came as a shattering disillusionment.

In 1915 Dr. Hamilton accompanied Jane Addams through the warring countries of Europe visiting all capitals, excepting Petrograd, in an effort to end the war by neutral arbitration. After the armistice, and before the peace treaty was signed, she attended with Jane Addams the International Congress, at Zurich, of the League for Peace in which German and Austrian women participated. In 1919, after the peace treaty, Alice Hamilton and Jane Addams with the backing of Herbert Hoover and the Quakers made a first-hand study of the effects of starvation upon the Germans, particularly the German children. Appointed the only woman member of the Health Committee of the League of Nations in 1924, she had the privilege of participating for several years in a program of international

cooperation in the field of public health. This included the control of epidemic and endemic diseases throughout the world—malaria, small pox, sleeping sickness, tuberculosis, leprosy, etc.—reduction in infant mortality, control of the opium trade and many other problems. She had the privilege of watching one government after another overcoming initial apathy and finally coming to the League of Nations for assistance. During those years, Dr. Hamilton visited and re-visited many European countries; followed their industrial development, their industrial hygiene techniques, their labor movements, and their labor legislation. In 1929, she was invited by the Department of Health in Russia to make a survey of its industrial hygiene program. In 1932, she visited Germany where she saw the beginnings of Hitler's "terror" and again in 1938 during "Munich week."

In 1919, Alice Hamilton was given the great honor of being appointed assistant professor of industrial medicine at Harvard. The break with tradition in appointing a woman to the faculty seemed incredible at that time, and she recalls for us some amusing limitations with which the appointment was hedged: she must not insist on her right to use the Harvard Club; she would not demand her quota of foot-ball tickets, etc., etc. During the years which followed, her students had the rare privilege of learning first-hand from her vast store of knowledge in this very young branch of medicine, and of benefiting from her interpretation of her unique experience, and from her wisdom. In 1935, Harvard "made me a Professor Emeritus which was a great honor and pleasantly ignores my sex."

During her professorship at Harvard, Alice Hamilton made her home with Dr. and Mrs. E. A. Codman, who lived in "one of those stately houses" along Beacon Street, Boston, "with two great rooms on each floor and endless stairs to reach them." They were kindred spirits, with their idealism and crusading zeal, and became fast friends. Together they worked tirelessly in many of the liberal causes of that period. To Mrs. Katherine Bowditch Codman, Alice Hamilton is "one of the loveliest women I have ever known."

In 1935, as Professor Emeritus, Alice Hamilton went to live in Hadlyme, Conn., a small picturesque village with many happy associations. She had purchased a charming house there years before as a home for the family to replace the Hamilton home in Fort Wayne, Indiana when it was sold. And there, usually with her sister Margaret, she has become deeply

rooted in the life of the local community. She enjoys the good New England town meetings, where she can participate in democracy in action at the grass roots. Gardening and sketching have been favorite pastimes.

During the years that she has lived in Hadlyme, Alice Hamilton, has, however, continued to keep in close touch with industrial hygiene both here and abroad and has been frequently called upon as a consultant. In 1935, for example, she was medical consultant to Frances Perkins, then Industrial Commissioner in New York State. In 1937 she made her study of carbon disulphide poisoning in the rayon industry; and in 1938 she read a paper on the subject in Germany at a meeting of the International Congress of Occupational Accidents and

Diseases. In 1939 she revised her *Industrial Toxicology*. She is always ready to "put in one more hour" when others would call it a day. She was instrumental in bringing Dr. Ludwig Teleky and his wife here out of Hitler's Germany. When Dr. Teleky was ill and alone, after his wife's death, she made him unbelievably happy by coming to see him in New York City, though it meant climbing many flights of stairs to reach his apartment. She was a model patient, cheerful, cooperative and optimistic, and made a remarkable recovery from a broken hip, a couple of years ago. She will never grow old.

Dr. Alice Hamilton is one of America's great women. It is with deep emotion that we honor her on her ninetieth birthday.

INDUSTRIAL HYGIENE NEWS REPORT

THE FIRST issue of a new publication, *Industrial Hygiene News Report*, appeared in October, 1958. This new and different publication is published independently by Flournoy and Associates with Howard N. Schulz, a former editor of the *AIHA Quarterly*, as Consultant Editor. The *Report* is to be issued monthly in a four-page news-letter format.

Among the subjects to be given attention in the *Report* are precautions for the safe handling of hazardous materials, experiences with unusual exposures, control of hazards from ionizing radiation, modifications of standard industrial hygiene equipment, new analytical methods, toxicological tests being conducted, methods for obtaining representative industrial hygiene samples, air pollution problems, noise control methods, and other data of interest. Also to be included are announcements regarding personnel changes in industrial hygiene units, meetings of national related associations, and developments in instrumentation. Reports are to be brief in order to permit prompt publication of current information in as many areas as possible.

Items and inquiries should be addressed to Industrial Hygiene News Report, 1791 West Howard Street, Chicago 26, Illinois.

Nitrogen Dioxide Indicator

JOHN R. KINOSIAN, B.S., and BYRON R. HUBBARD, M.A.*

California State Department of Public Health, Berkeley, California

THIS paper describes a simple device for the rapid detection and semiquantitative determination of trace quantities of nitrogen dioxide (NO_2) in air. Essentially, the device consists of a glass tube filled with silica gel impregnated with sulfanilic acid, and N-(1-naphthyl)-ethylenediamine dihydrochloride. When air is passed through this reagent column, even minute amounts of NO_2 in the air are adsorbed on the reagent, and an intense red stain is formed. The length of the stain produced is a function of, and is used to measure the concentration of NO_2 in the sample.

Previously Developed Methods

The use of silica gel in analytical methods for NO_2 is not new. Among the papers on this subject are those by Flagg and Lobene¹ and by Wade, Elkins, and Ruotolo.²

Flagg and Lobene removed small concentrations of NO_2 from air by passing the mixture through a column of silica gel where the NO_2 was adsorbed. Next they attempted to estimate the quantity of NO_2 adsorbed in this procedure by passing diphenylamine reagent (dissolved in water and H_2SO_4) through the adsorption column. This procedure produced a colored stain on the column, but due to the washing action of the reagent, the stain length could not be used for a quantitative estimate of the adsorbed NO_2 .

They then transferred the silica gel with adsorbed NO_2 from the sampling column to a porcelain dish and treated it with diphenylamine reagent. There they obtained a blue color resulting from the reaction of NO_2 with diphenylamine reagent, and by measuring the intensity of color developed, they were able to measure the quantity of NO_2 adsorbed on the silica gel.

Wade, Elkins, and Ruotolo utilized the adsorption of NO_2 by silica gel in a different way. By passing mixtures of NO_2 , NO, and air through a column of silica gel, they selectively adsorbed the NO_2 . Following this separation, they determined the quantity of NO_2 on the

silica gel by the phenoldisulfonic acid method. The unadsorbed NO-air mixture which passed through the silica gel was collected, the NO was oxidized to NO_2 , and this product was in turn determined by the phenoldisulfonic acid method. Using this procedure, they were able to obtain much valuable information about the quantity and relative proportions of NO and NO_2 produced by various industrial processes such as carbon arcs, oxyacetylene torches, Diesel motors, dynamite blasting, and in the combustion of cellulose nitrate.

Other, and perhaps more widely used methods of analysis for oxides of nitrogen include:

The phenoldisulfonic acid method reported by Beatty, Berger, and Shrenk.³ In this method a sample of the air is obtained in a glass sampling bottle. Traces of oxides of nitrogen in the sample are absorbed by means of a concentrated sulfuric acid-hydrogen peroxide reagent. Phenoldisulfonic acid reagent and sodium hydroxide are then added and the presence and amount of NO_2 is determined by the intensity of yellow color formed. This method indicates the total of all nitrogen oxides except N_2O . It is not specific for NO_2 . Although a long period for absorption and analysis is required, the method is regarded as being very satisfactory for the determination of total nitrogen oxides, and it has been widely used by industrial hygienists.

On the other hand, to fill the need for a more rapid field sampling method for oxides of nitrogen, Patty and Petty⁴ developed a syringe sampling device containing a modified Griess-Ilosvay reagent. The quantity of NO_2 in a sample of air drawn into the syringe is estimated from the intensity of the red color developed with the reagent. This method is rapid and has been successfully and extensively used by industrial hygienists.

Saltzman⁵ adapted the use of a more stable modified Griess reagent^{6, 7, 8, 9}, sulfanilic acid and N-(1-naphthyl)-ethylenediamine dihydrochloride, to the microdetermination of nitrogen dioxide in air.

Griess reagents are specific for NO_2 ; however nitric oxide may interfere as it is oxidizable by oxygen in air to nitrogen dioxide. If air

* Industrial Hygiene Engineer and Chief Industrial Hygiene Engineer, respectively. Submitted through William H. Clark, M.D., Chief, Bureau of Adult Health, Division of Preventive Medical Services.

samples are collected in syringes or bottles and are retained, concentrations of NO_2 will be higher than existed at the time of sampling due to NO_2 formation from nitric oxide.

Direct Indicator Method

Although sensitive and accurate methods, such as those which have been cited, are available for the determination of oxides of nitrogen, an even more rapid and specific method for detecting and estimating NO_2 in air, and one requiring only moderate laboratory skills, has been sought for rapid field use. The method presented here is somewhat similar in form to the existing rapid and simple methods for estimating carbon monoxide, aromatic hydrocarbons, and sulfur dioxide by means of a colored stain developed on a column of silica gel reagent.

The reagent used in this method for NO_2 is prepared by impregnating silica gel with sulfanilic acid and N-(1-naphthyl)-ethylenediamine dihydrochloride. When this reagent is packed into a glass tube, and air containing a trace of NO_2 is drawn through the tube, the NO_2 in the air is adsorbed on the reagent where a diazotizing and coupling reaction takes place to form a red stain. By standardizing the reagent preparation, the cross-sectional area of the reagent column, the volume of air sampled, and the sampling rate, it is possible to utilize the length of stain formed on the reagent column to estimate the concentration of NO_2 in the air sampled.

Reagent Preparation

One hundred grams of 28- to 35-mesh silica gel is wetted uniformly with a freshly prepared solution of 1% sulfanilic acid and 0.08% N-(1-naphthyl)-ethylenediamine dihydrochloride. The solution is added slowly with constant stirring until the silica gel appears thoroughly moistened. Forty to 80 ml of the solution is required per 100 grams of the silica gel.

The reagent gel is then placed in a desiccator containing calcium chloride desiccant. In a period of from 24 to 48 hours the product should appear dry, granular, "free running" like sugar, and preferably white. It is then transferred to a tightly-stoppered, dark-colored bottle for protection from light, water vapor, and NO_2 . Reagent gel prepared in this manner and kept in a refrigerator has remained perfectly stable for three months, and it is believed that it could be stored for a considerably longer period of time without deterioration.

Preparation of Indicator Tubes

Indicator tubes are prepared from glass tubes 12 centimeters long and 3.0 millimeters inside

diameter. A piece of glass cloth about 1 cm square is pushed about 3 cm into the end of one of the tubes as a porous plug. Silica gel reagent is then poured into the opposite end of the tube to a point about 3 cm from the top. This provides a column of silica gel approximately 6 cm in length. Another plug of glass cloth is then pushed down into the top of the tube to hold the silica gel reagent in position.

Following this, the tube is held vertically and gently tapped against the table top. This will pack and level the surface of the reagent. The upper glass plug is firmly pushed down against the level surface of the reagent. The tube is then inverted and a similar cycle of tapping, packing, leveling, and pushing the porous plug firmly into place is completed.

Careful and uniform packing produces a face (where the plug and reagent meet) that is plane and perpendicular to the tube axis. This is important because it aids in obtaining a stain that is of equal length on the various sides of the column, and such a stain is desired because it can be measured with greater accuracy.

Sampling tubes are easily filled by means of a small bottle fitted with a rubber stopper through which a small hole has been bored. Silica gel reagent in the bottle can easily be poured directly into a sample tube placed in the hole.

Pumping and Metering Apparatus

Sampling can be accomplished with any source of vacuum, and a small flowmeter suitable for metering air through the sampling tubes. For field sampling, a simple rubber bulb fitted with a rapid air release valve and a capillary to regulate the rate of inward airflow, has been found quite satisfactory. (Figure 1.) For this work short pieces of glass and rubber tubing were used to connect a glass tee with a 50 ml laboratory type rubber bulb. A pinch clamp on a piece of rubber tubing fitted on the side arm of the tee provided a quick air release valve. The remaining open end of the tee was then connected with the capillary by a short length of rubber tubing. The open end of the capillary was also fitted with a short length of rubber tubing for connection with successive sampling tubes.

Sampling with this apparatus is accomplished by expelling air from the bulb through the side arm valve, closing the pinch clamp, and allowing the bulb to expand and consequently to draw a 50 ml air sample inward through a sampling tube and the capillary. Sampling from a tank is accomplished by connecting the open end of the sampling tube to the tank with a short piece of rubber tubing.

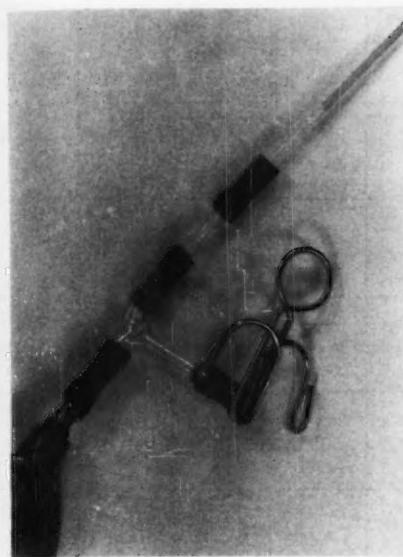


FIGURE 1. Sample metering device.

The capillary chosen had a high resistance compared with sampling tubes, and thus served to maintain a very constant rate of flow, regardless of any possible small changes in resistance of sampling tubes. With the bulb and capillary used, the time for the bulb to fully expand was fixed at 34 ± 3 seconds or at an approximate average rate of 90 ml per minute.

In practice, four bulb volumes or 200 ml of air were drawn through the sampling tube for each sample. This volume and sampling rate were chosen somewhat arbitrarily and on an empirical basis for the range of concentration (1-50 ppm) of NO_2 under consideration; and calibration can, of course, be made for other rates and sample volumes.

Preparation of Known Concentrations

Standard concentrations of NO_2 were prepared in stainless steel oxygen tanks ('34 liters volume) obtained from war surplus. Each tank was fitted with a needle valve and hose connector. Steel tanks were used in preference to glass tanks, since there is some indication that adsorption of nitrogen oxides by glass surfaces may take place.⁶ Two alternate methods of preparing known concentrations of NO_2 in the tanks have been employed.

In the first method, a measured volume of NO_2 gas was introduced directly into a completely evacuated tank which was then allowed to draw in air until pressure equilibrium with

the atmosphere was reached. The NO_2 concentration in the tank was then calculated, and the calculation checked by withdrawing a carefully measured volume of the mixture and analyzing it for NO_2 by the Saltzman method.⁵

The second method of preparing NO_2 concentrations is similar to the first, except that NO was substituted for NO_2 . NO is oxidized by air according to the equation:



The velocity of this reaction in air has been shown to be $dc/dt = -kc^2$, where c is the concentration of nitric oxide.¹⁰ Figure 2, based on a rate constant value of $k = 3 \times 10^{-4} \text{ ppm}^{-1} \text{ min}^{-1}$, illustrates the increase of NO_2 with time at various initial concentrations of NO.

NO_2 atmospheres prepared by the second method were, as in the first case, established by both calculation and by frequent analytical checks using the Saltzman method of analysis.

Calibration of Indicator Tubes

The tubes are calibrated by drawing 200 ml (four pumping cycles of the 50 ml bulb) of the known NO_2 concentrations through the tubes at a rate of approximately 90 ml per minute. The stain length is then carefully measured and is plotted as a function of the logarithm of the NO_2 concentration. Figure 3 illustrates the results of calibration of three tubes, each at four different concentrations of nitrogen dioxide.

Determinations with Indicator Tubes

To measure unknown NO_2 concentrations in the atmosphere, a sampling tube is connected to the pumping device and 200 ml of air is drawn through the tube at the same rate employed for calibration (90 ml per minute). The length of the stain that is formed is then measured, and the NO_2 concentration is obtained from the calibration curve (Figure 3).

Interferences and Variations

Saltzman studied the possible interference of other gases with the sulfanilic acid, N-(1-naphthyl)-ethylenediamine dihydrochloride, acetic acid, NO_2 color-forming reaction. Ozone, sulfur dioxide, nitrogen oxides (other than NO_2), hydrogen sulfide, chlorine, hydrogen peroxide, and formaldehyde were included in his study. Of these, ozone and chlorine were found to produce some interference. However, this interference was not serious, except when the concentration of interfering gases greatly exceeded that of NO_2 .

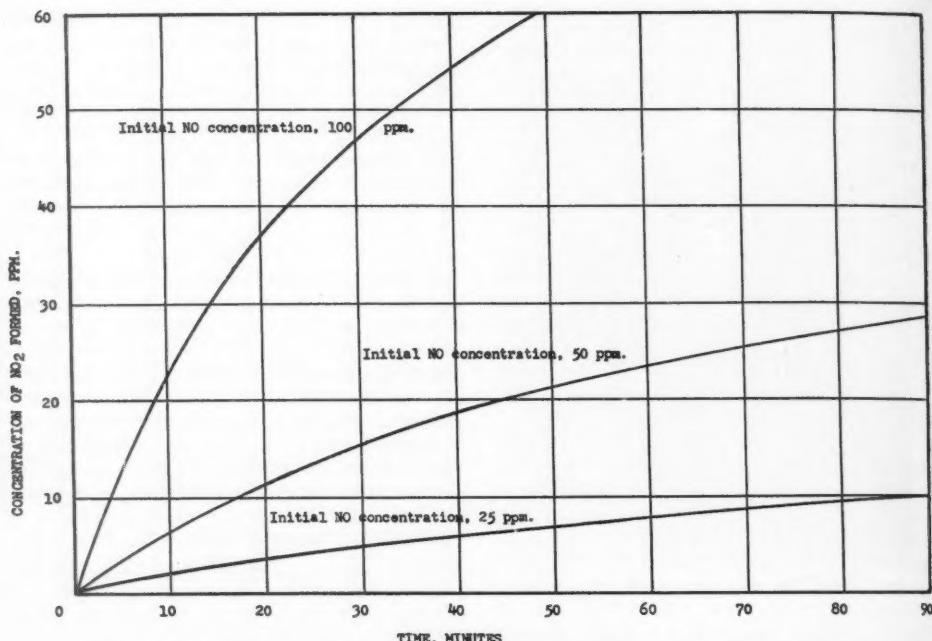


FIGURE 2. Concentrations of nitrogen dioxide formed with time from several nitric oxide concentrations.

When NO₂ silica gel reagent stains were exposed to ozone and chlorine there were no observable effects. From this and other observations, it is believed that ozone does not interfere even if it is mixed and sampled with NO₂. However, the difficulty of establishing quantitative mixtures of the several gases prevented an exhaustive investigation of this question.

Increasing the volume of sample passed through an indicator tube, with other factors constant, results in a longer stain. Data illustrating the stain length versus volume relationship appear in Figure 4.

Increasing the flow rate, with volume and other factors constant, also results in a longer stain. Data illustrating the stain length versus flow rate relationship appear in Figure 5.

Although this method was developed primarily for industrial hygiene work with a primary interest in NO₂ concentrations between 1 and 50 ppm, it should be noted that by using a longer sampling time and consequently a larger sample volume, it is possible to detect and estimate NO₂ concentrations down to or below several tenths of a part per million. From this standpoint the device may have application to air pollution problems.

Shorter stain lengths are produced when the NO₂ air mixtures and sampling apparatus are cooled substantially below room temperature (ca 74°F). For example, at 39°F the concentration indicated by the device is approximately one-half that which would be indicated at room temperature (74°F). In other words, if a concentration of 10 ppm at 39°F is sampled, a stain of approximately 1.6 cm is formed. Referring to Figure 3, it is evident that a stain of this length corresponds to 5 ppm rather than the 10 ppm which was actually sampled.

Increasing the temperature from room temperature to 90°F seemed to have no significant effect on the stain length.

Small variations in humidity do not appear to cause any significant effect on results, although some error due to extreme variations in humidity are not ruled out.

Discussion

Measurement of stain length is one of the most critical operations in obtaining accuracy with this method. The difficulty in stain length measurement arises largely because the stain does not end in a sharp boundary, but gradually

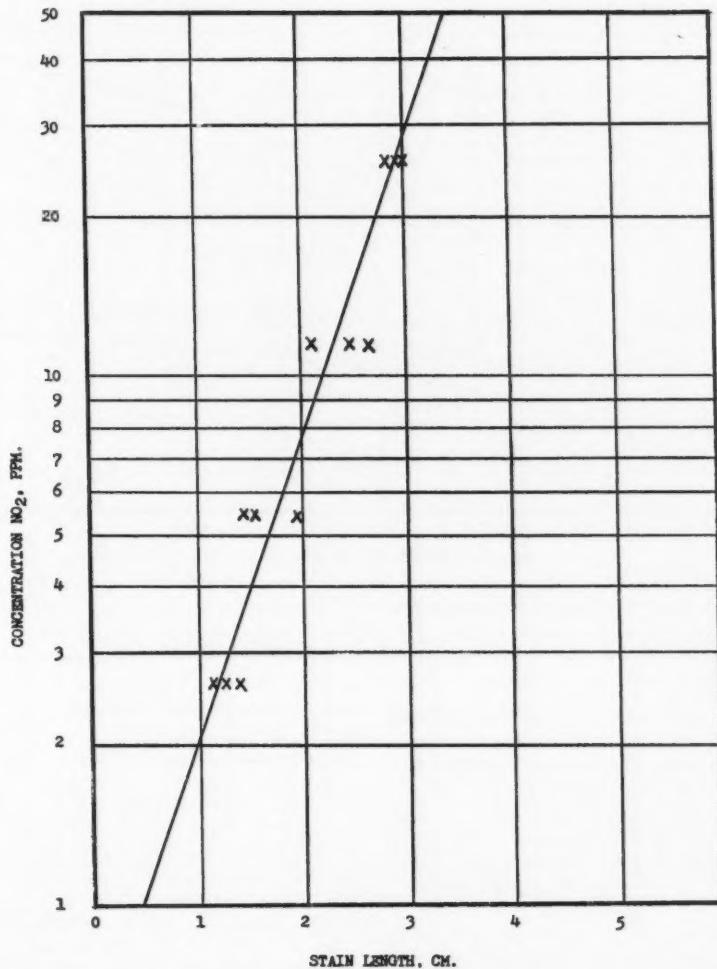


FIGURE 3. Calibration of indicator tubes.

diminishes from red to pink to white over a distance of several millimeters along the column. The stain lengths in Figure 3 were measured to the extremity of the stain, that is, to the point where the pink color was no longer perceptible.

There seems to be no simple and precise manner to overcome this difficulty. However, it can be minimized if each person prepares his own calibration curve, and thereafter is careful to read the end point consistently. Life size color photographs of calibrated tubes can also aid in establishing the end point.

Figure 6 illustrates how tubes may be used

as standards; however, the black and white photograph does not fully show the character of the diminishing color at the end point.

A variety of different proportions of sulfanilic acid and N-(1-naphthyl)-ethylenediamine dihydrochloride, and also a variety of different proportions of the total color-forming reagent to silica gel were prepared and tried. Of all the various proportions tried, the one given in this paper appeared to give the most satisfactory results.

The particle size of the silica gel used was found to be of considerable importance, since "fines" remaining in the gel tend to alter the

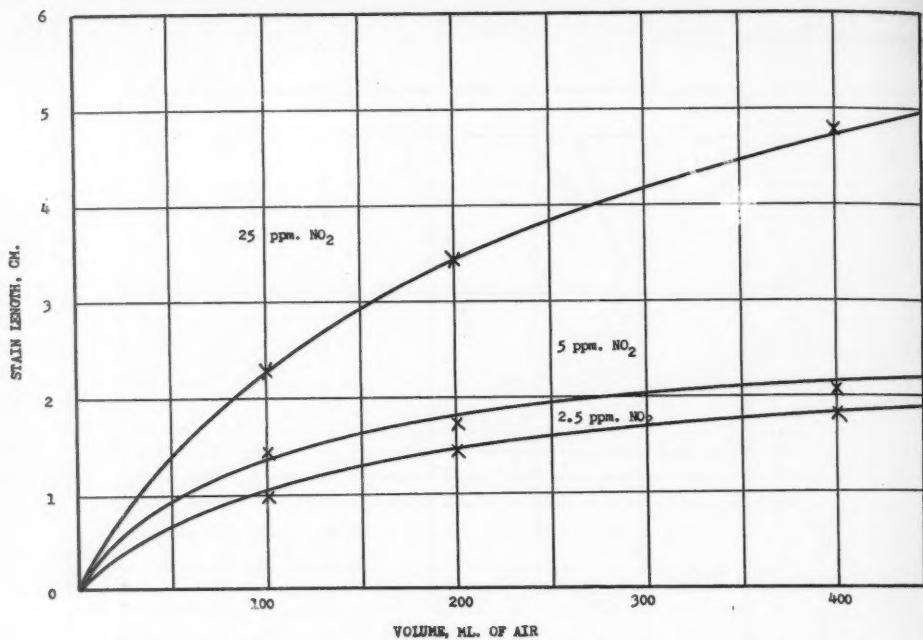


FIGURE 4. Effect of volume of air sampled on the stain length. (Air drawn through the tubes at the rate of 90 ml per minute.)

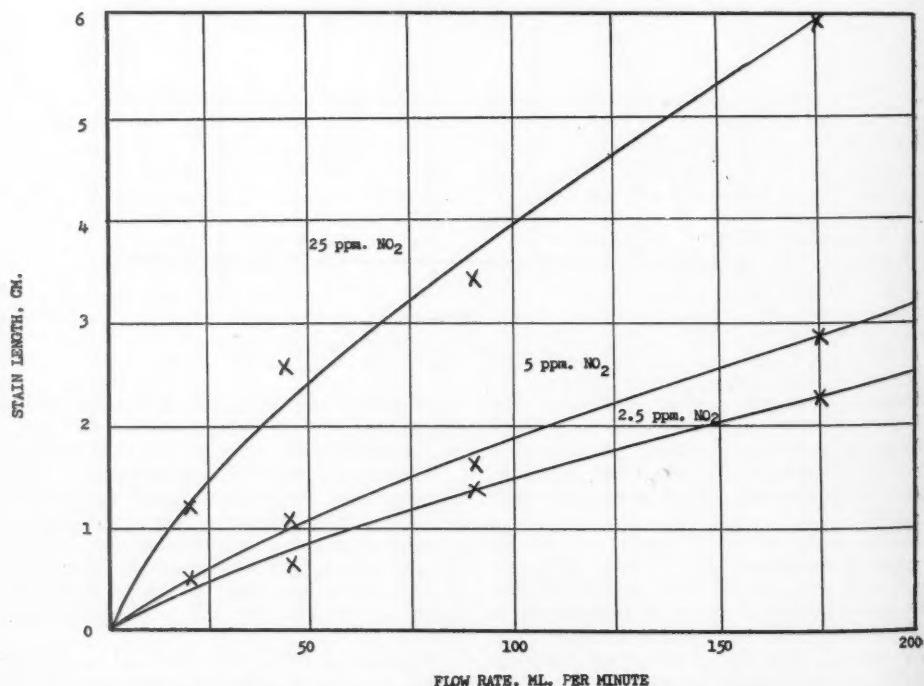


FIGURE 5. Effect of flow rate on the stain length (200 ml of air drawn through the tubes).

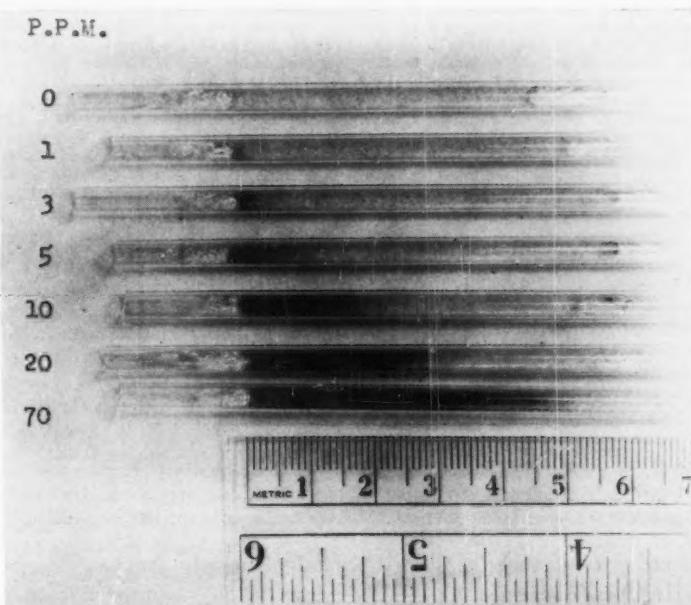


FIGURE 6. Illustration of the stains formed in the indicator tubes from concentrations of nitrogen dioxide.

flow rate through the column. Also, "fines" have a tendency to collect on one side of the tube, and this in turn appears to cause "channeling" of the sample flow through the column, which results in the formation of a stain with different lengths on different sides of the tube. Although the length of a stain may be measured by averaging the short and long side, the most precise measurements are obtained when stain lengths are nearly uniform in length on all sides of the column of silica gel.

Silica gel reagent dried in a desiccator over sulfuric acid produces a barely preceptible and unsatisfactory depth of red color when exposed to NO_2 . Reagent dried in the oven at 180°F becomes brown and unusable. Reagent dried in the open air develops a red color on the surface while drying, probably due to NO_2 in the air, but seems to work quite well when the red surface portion has been removed or diluted by mixing with the remainder of the material.

The most satisfactory reagent from the standpoint of color, sensitivity, and uniformity, is obtained when the reagent is dried in a closed desiccator over a good quality calcium chloride drying reagent. Different batches of reagent prepared in this manner appear to have negligible differences in adsorption and color-forming properties.

Summary

A rapid, simple, and convenient semiquantitative method for the determination of NO_2 in air has been developed. The method does not appear to be susceptible to interference from nitric oxide (NO) or other gases commonly found in industry.

The method as presented will determine NO_2 concentrations in the range of from 1 to 50 ppm with an accuracy of $\pm 50\%$, but with further refinements the accuracy can be increased. By sampling larger volumes of air, concentrations of NO_2 less than 1 ppm can be determined.

Acknowledgments

The permission and encouragement of Dr. William Clark, Chief, Bureau of Adult Health, which made possible the utilization of laboratory equipment and time for the development of this method is both acknowledged and appreciated. We also wish to thank Mr. William Thielen, Public Health Chemist, for the preparation of known nitrogen dioxide concentrations.

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TRAINING COURSES

THE U. S. Public Health Service, Robert A. Taft Sanitary Engineering Center in Cincinnati is offering a number of special courses in various aspects of air pollution control and radiological health. Dates and course for the immediate future are:

- January 12 through 23, 1959—Chemical Microscopy for Analysis of Air Pollutants
- January 12 through 23, 1959—Basic Radiological Health
- January 26 through 30, 1959—Radioactive Pollutants in Air
- February 9 through 20, 1959—Community Air Pollution
- February 16 through 20, 1959—Radioactive Pollutants in Water
- March 16 through 20, 1959—Physical Analysis of Atmospheric Particulates
- March 23 through 27, 1959—Analysis of Atmospheric Inorganics

Personnel from health, control, educational, research, and industrial groups will be enrolled by application. There are no tuition fees. For additional information write or call Chief, Air Pollution Training, Training Program, Robert A. Taft Sanitary Engineering Center, 4676 Columbia Parkway, Cincinnati 26, Ohio. (Phone TRinity 1-1820)

INDUSTRIAL VENTILATION CONFERENCE

THE EIGHTH Annual Industrial Ventilation Conference will be held in East Lansing, Michigan, February 16 through 19, 1959. This annual conference is jointly sponsored by the Division of Occupational Health, Michigan Department of Health and the Department of Mechanical Engineering and Continuing Education Services, Michigan State University. Workshop groups will study problems of design and ventilation for mining, manufacturing, and other industrial applications. Informal lectures and demonstrations will include: air flow fundamentals, testing of exhaust systems, fan selection and application, collector performance, and make-up air applications.

For complete information write to Eighth Annual Industrial Ventilation Conference, Continuing Education Service, Michigan State University, East Lansing, Michigan.

Direct Determination of Boranes by the Carmine Method*

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DURING THE early stages of development in the field of boron-hydrogen compounds, analytical methods were restricted to hydrolysis or pyrolysis of relatively large amounts of substance with subsequent determination of boric acid or hydrogen by macro techniques.⁵⁻⁸ At a later date the need for micro methods became apparent especially with the advent of toxicological investigations of this class of compounds, and some methods for the direct analysis of boranes were published.²⁻⁴ The standard curves required by these methods are only as good as the purity of the chemicals used for obtaining them, and thus there remains the need for a simple method for checking on reputed concentrations of solutions used for standardization, one that would preferably be simple enough to permit its use in laboratories that might not have the most modern instrumentation.

It has been found that boranes can be determined in micro quantities by the Carmine method of borate analysis.¹ A solution of the borane, in suitable concentration, is introduced into concentrated sulfuric acid in the same manner in which the standard boric acid solution or the unknown borate containing solution is now introduced. Then the solution of Carmine in concentrated sulfuric acid is added and the color produced is determined spectrophotometrically.

Equipment and Reagents

Coleman Junior Spectrophotometer 6B, with constant voltage transformer. Matched ($\pm 0.5\%$) glass stoppered tubes with standard taper 14/20 stoppers, made of Pyrex culture tubes, Corning Catalog No. 9820, without rim, size 18 x 150 mm. Boron-free tubes would be preferable but cannot be fitted with glass stoppers.

Carmine No. 40 N.F., Fisher Scientific Company Catalog No. C-195—0.5 gram per liter of concentrated sulfuric acid.

* The work reported in this paper was sponsored by the Gellery Chemical Company under a contract from the Bureau of Aeronautics, Department of the Navy.

Procedure

The borane in question is dissolved in water, with or without the aid of a solubilizing agent, so that the stock solution contains somewhere between 50 and 200 micrograms of boron per milliliter. Dilutions are then prepared to represent 1, 2, 5, 8, and 10 micrograms of boron per ml. From each dilution one ml is pipetted into the Carmine tubes, whereupon 5 ml of concentrated sulfuric acid is added and then 5 ml of Carmine reagent. If nitrates are suspected to be present, a few drops of concentrated hydrochloric acid are added, as specified by Hatcher and Wilcox.¹ After one hour the colors thus produced are compared at a wavelength of 625 millimicrons with a standard curve obtained in a similar manner, but using boric acid standard solutions. Blanks are prepared in exactly the same manner as the standards and the unknowns. They compensate in a large measure for the insignificant amounts of boron extracted from the Pyrex glass tubes by the reagents employed. For "unknown" boranes or their solutions it is generally necessary to prepare several dilutions in order to get into the proper range of concentration in which the method is applicable, namely about 1-10 micrograms of boron per ml of solution tested.

Results

The method was applied to dimethylamine-borane ($(CH_3)_2NH \cdot BH_3$), trimethylamine-borane ($(CH_3)_3N \cdot BH_3$), pyridine-borane $C_6H_5N \cdot BH_3$ and to decaborane $B_{10}H_{14}$, and the results obtained are given in Tables I-IV. It is seen that the method is applicable to the four boranes studied. Accuracy is best for dimethylamine-borane, ranging about 2%, next best for pyridine-borane, ranging about 4%, and poorest for trimethylamine-borane and decaborane, with deviations of about 5-7%. These averages leave out the one microgram level for which the averages range about 15%, probably due to the insufficiency of the spectrophotometer at this level (transmittances of 90% and over), but

TABLE I
Analyses of Dimethylamine-borane

Date	Solutions used	Micrograms of boron found for theoretical				
		1γ	2γ	5γ	8γ	10γ
8-8	Fresh stock sol., diluted	0.9	1.9	4.9	7.5	9.6
8-9	Dilutions of 8-8	0.9	1.9	4.0	7.6	9.7
8-19	Fresh dil. from stock sol. of 8-8	0.9	2.0	5.1	8.0	9.9
8-30	Fresh stock sol., diluted	0.8	1.9	5.0	8.0	9.8
9-6	Fresh stock sol., diluted	0.8	2.0	5.0	8.0	9.6
9-6	Fresh dilution from stock sol. of 8-30	0.9	2.0	5.1	8.0	9.5
9-13	Fresh dilution from stock sol. of 9-6	0.8	2.0	5.2	8.0	10.0

TABLE II
Analyses of Pyridine-borane

Date	Solutions used	Micrograms of boron found for theoretical				
		1γ	2γ	5γ	8γ	10γ
8-8	Fresh stock sol., diluted	0.9	1.9	4.8	8.0	9.9
8-9	Dilutions of 8-8	0.9	1.9	5.0	8.2	9.5
8-19	Fresh dilution from stock sol. of 8-8	0.9	2.0	5.0	8.2	9.9
8-31	Fresh stock sol., diluted	0.8	1.8	4.9	7.6	9.5
9-6	Fresh stock sol., diluted	0.8	1.8	4.9	8.0	9.5
9-7	Fresh dilution from stock sol. of 8-31	0.8	1.8	5.0	7.7	9.4
9-13	Fresh dilution from stock sol. of 9-6	0.9	2.0	5.1	8.0	9.8

TABLE III
Analyses of Trimethylamine-borane

Date	Solutions used	Micrograms of boron found for theoretical				
		1γ	2γ	5γ	8γ	10γ
8-8	Fresh stock sol., diluted	0.9	1.7	4.6	7.3	8.5
8-9	Dilutions of 8-8	0.9	1.9	5.0	8.2	9.5
8-19	Fresh dilutions from stock sol. of 8-8	0.8	1.8	4.6	7.3	8.8
9-1	*Fresh stock sol., diluted	0.9	1.9	4.9	7.5	9.3
9-7	Fresh stock sol., diluted	0.8	1.9	5.0	7.7	9.7
9-8	Fresh dilutions from stock sol. of 9-1	0.8	1.9	4.9	7.5	9.2
9-14	Fresh dilutions from stock sol. of 9-7	0.9	1.9	4.7	7.8	9.4

*Stock solution made from recrystallized compound

possibly because of the variable pickup of boron from the Pyrex glass tubes.

A comparison was made of this method with a procedure that might be considered standard, i.e., slow hydrolysis of the borane in acid methanol (in a distilling flask), distillation of the

TABLE IV
Analyses of Decaborane

Date	Solutions used	Micrograms of boron found for theoretical				
		1γ	2γ	5γ	8γ	10γ
8-19	Fresh stock sol., diluted	0.8	1.8	4.6	7.3	9.1
8-30	Fresh dilutions from stock sol. of 8-19	0.8	1.8	4.9	7.7	9.4
9-7	Fresh stock sol., diluted	0.7	1.8	4.8	7.6	9.3
9-8	Fresh stock sol., diluted	0.9	1.9	4.9	7.5	9.2
9-14	Fresh dilutions from stock sol. of 9-7	0.9	2.0	4.9	7.6	9.3
3-20	Fresh stock sol., diluted	0.8	1.9	4.8	7.7	9.5

TABLE V
Analyses of Dimethylamine-borane
(coded as an "unknown" containing 25% B)

Amount of boron, micrograms	Amount of boron found, micrograms		
	Assumed	Theoretical	Carmine Method
10	7.3	7.1	
10	7.3	7.1	
10	7.3	7.2	
10	7.3	7.1	
10	7.3	7.0	
10	7.3	7.3	
10	7.3	7.0	
5	3.65	3.5	
5	3.65	3.7	
20	14.6		12.7
20	14.6		13.3
10	7.3		6.1
10	7.3		5.6

boron as methyl borate, and subsequent Carmine analysis. The results are given in Table V. It is seen that the new method is much more accurate than the methyl borate distillation which has always given low results in this laboratory. In carrying out this work the analyst had not been told what the compound was, but had been given to understand that it contained 25% boron. It is on this basis that the figures in the first column, captioned "Assumed" had been based. The theoretical concentrations were calculated on the basis of the true boron content of dimethylamine-borane, which is 18.3%.

Discussion

Solubilizers: Some of the boranes, such as dimethylamine-borane, dissolve well in water, and no difficulty is encountered in preparing solutions from them. In other cases it is necessary to bring the compound into solution with the aid of solvents or alkali. In the case of

pyridine-borane, for instance, 0.4258 gram of the compound was dissolved in 10 ml of propylene glycol, and the solution was diluted with water to the desired concentrations. Decaborane is best dissolved in a mixture of 10 ml ethanol and 10 ml of 0.6 N NaOH and then diluted to the desired volume. Other solvents or alkaline materials can be used if they do not produce a discoloration on addition to concentrated sulfuric acid.

Limitations: The method cannot be used for boranes which give colored solutions with concentrated sulfuric acid, which could conceivably be the case if the borane carries a heavy organic "tail". In the work here reported no such discolorations have been observed, neither with the boranes nor with the amine portions of the compounds when the latter were tested by themselves. Gaseous and low boiling boranes can be handled only if they can be absorbed in concentrated sulfuric acid, an alkali, an amine or other suitable solvent. For instance, it has not been possible so far to apply the method to pentaborane (B_5H_9) because this compound does not dissolve easily in the ordinary solvents. Attempts to remove it from the exit air of animal exposure chambers by means of alkali, triethanolamine, xylene and even concentrated sulfuric acid were unsuccessful because of incomplete absorption. The method is non-specific since it is based on a measurement of the boron content and not the borane itself. For this reason, it cannot differentiate between several boranes in a mixture, nor between boranes and boric acid or boric oxide contained in the samples as impurities.

Time Requirement: In viewing the results obtained with decaborane (Table IV) it was considered possible that the low results might be due to the known slowness of hydrolysis of this compound. However, this was not found to be a proper explanation when the decaborane solutions were first added to the concentrated sulfuric acid and allowed to stand for periods of 5½ and even 24 hours before addition of the Carmine reagent. Results obtained in this man-

ner were not substantially different from those reported in Table IV. The customary waiting period of 60 minutes, normally employed before reading the Carmine colors, apparently was sufficient to permit complete hydrolysis of the boranes investigated.

Further Developments: Many of the amine-boranes are well crystallized materials of good stability. In view of the poor quality of boric acid and boric oxide as primary boron standards it has occurred to the authors that some of the amine-boranes might be very useful for the latter purposes. This possibility will be tested as time permits.

Summary

It was found possible to determine boranes at microgram levels by introducing their aqueous solutions into concentrated sulfuric acid and addition of a solution of Carmine in concentrated sulfuric acid. The resultant color is measured by means of a spectrophotometer. The method is non-specific and will not differentiate between boranes and e.g. boric acid or boric oxide.

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Determination of Thorium in Urine*

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Introduction

THERE IS some evidence that the use of the thorium content of urine is not a reasonable estimate of exposure level. Many installations, however, use a positive value of thorium in urine to indicate that some exposure has taken place.

One estimate based on the biochemical similarity of thorium to plutonium¹ indicates that the minimum sensitivity required to study the excretion rates and body burden is 0.2 microgram of thorium per liter of urine. Several of the existing spectrophotometric methods based on the reaction of thorin and morin are capable of detecting this quantity of thorium in pure solution.^{2, 3, 4, 5, 6} These reagents are not specific for the thorium ion and isolation of thorium is necessary prior to its determination. Existing methods for the isolation of thorium from various matrices are based on the following reactions:

- (1) Coprecipitation with lanthanum fluoride and thenoyltrifluoroacetone extraction.²
- (2) Coprecipitation of thorium and calcium as the oxalate.⁷
- (3) Oxalate precipitation and a mesityl oxide extraction.⁸
- (4) Ion exchange separation with a thenoyltrifluoroacetone extraction.⁹

Thorium, a quadrivalent ion, is adsorbed readily by cation exchange resins and the most commonly used inorganic eluting agent, hydrochloric acid, does not readily remove this element from the resin. This fact should enable the development of a simple and rapid method for the separation of thorium, from the other ionic constituents of urine.

Sulfate and phosphate anions in urine complicate a direct ion exchange separation. Thorium forms numerous complexes with these anions. The valences of these complexes range from neutral to quadrivalent. Therefore, in any separation procedure based on valence the thorium ion is found in each fraction throughout the procedure.

* Presented at the annual meeting of the American Industrial Hygiene Association, April 24, 1958, Atlantic City, New Jersey.

The introduction of an oxalate precipitation step prior to the ion exchange procedure reduces the concentration of these anions so that the resin adsorbs the thorium ion.

Various organic reagents, including diammonium citrate,⁹ EDTA,¹⁰ and others, have been used to remove thorium from cation exchange resins. For our use, these reagents have two disadvantages, the large volume of reagent necessary to quantitatively elute thorium and the necessity of ashing the organic complex prior to the spectrophotometric determination.

Apparatus and Reagents

Beckman Model DU Spectrophotometer.

Beckman Model G pH Meter.

Thorin [O-(2-hydroxy-3,6-disulfo-1-naphthylazo) benzeneearsonic acid disodium salt], 0.1%. Dissolve 250 milligrams of thorin in 250 milliliters of distilled water.

Morin — (2',3,4',5,7-pentahydroxyflavone) 0.2%. Dissolve 500 milligrams of morin in 250 milliliters of ethyl alcohol.

Hydrochloric acid, 1N. Dilute 84 milliliters of concentrated hydrochloric acid sp. gr. 1.18 to one liter.

10% Oxalic acid. Dissolve 100 grams of oxalic acid in distilled water.

Dilute to one liter.

1% Oxalic acid wash solution. Dilute 100 ml of 10% oxalic acid solution to one liter.

Dowex 50 X-8 cation exchange resin, 200-400 mesh.

Sulfuric acid, 4M. Dilute 224 milliliters of concentrated sulfuric acid sp. gr. 1.84 to one liter.

Buffer solution. To 100 ml of e.p. o-toluidine, add 50 ml of purified perchloric acid and then two liters of redistilled water. After stirring, allow to stand for several hours and then decant. At this point, the pH is around 4.2 and the solution is still cloudy. By adding 400 ml more of water and 10 ml of purified perchloric acid, the solution is clarified and the pH is brought to 4.0. If the pH is not exactly 4.0, adjust with sodium hydroxide or perchloric acid. Store the solution in a brown bottle, away from direct sunlight.

Chrome Azurol S dye, (0.04%). Weigh 0.40 gram of Chrome Azurol S (Geigy) and dissolve in one liter of water containing 50 mg of thymol and 5.0 grams of gum arabic. Because the absorbance changes with time, finally approaching a constant value, the solution is allowed to stand for two to three weeks. Filter before use, and store in a brown bottle. Perchloric Acid (pH 1.0 and pH 2.0). Add reagent grade perchloric acid to distilled water until the required pH is reached.

Resin Preparation

Using a soxhlet extractor, extract 500 grams (wet weight) of Dowex 50 X-8 (200-400 mesh) overnight with two liters of methyl alcohol. Transfer the resin to a three liter beaker and wash with alternate two liter portions of 3*N* hydrochloric acid and 3*N* sodium hydroxide. Wash with two 2-liter portions of distilled water and transfer seven milliliters of wet resin to a standard ion exchange column 10 cm long and 1.4 cm inside diameter. Pass 250 milliliters of 1*N* hydrochloric acid through the resin column. The column is ready to receive the sample solution.

This procedure is recommended for commercially available ion exchange resin as small concentrations of metal ions interfere with the thorium determination.

Isolation Procedure

- Pour measured volume of urine into a centrifuge bottle.
- Adjust the urine to pH 8 or slightly higher, using ammonium hydroxide. Stir well while adjusting the pH.
- Centrifuge the sample for 15 minutes. Decant and discard the supernatant liquid.
- Dissolve the precipitate with 10-20 ml of concentrated HNO₃. Wash the solution into a 75 ml platinum crucible. Evaporate to dryness.
- Wet ash the residue with several additions of concentrated HNO₃ and evaporate to dryness.
- Dissolve the ashed residue in 100 ml of 1*N* HCl.
- Adjust the solution to pH 4 using sodium hydroxide. Use pH meter.
- Heat the solution to 95°C, then add with stirring 4 ml of a 10% oxalic acid solution.
- Stir vigorously until precipitate forms, then allow the solution to cool to room temperature.
- Filter by gravity through #42 Whatman filter paper.

- Wash the precipitate with a 1% oxalic acid solution.
- Transfer the filter with precipitate to a crucible and dry at 110°C, then ignite at 450-500°C.
- Dissolve the ash with a few ml of 1:1 HCl, evaporate on a sandbath and ignite again at 450-500°C.
- Dissolve the ash in a minimum of 0.5*N* HCl.
- Transfer the sample to a prepared resin column.
- Wash the column with 50 ml of distilled H₂O, then 50 ml of 3*N* HCl at a flow rate of 2 ml per minute.
- Elute thorium with 50 ml of 4*M* H₂SO₄. Collect in a 50 ml volumetric flask.
- Transfer the solution to a platinum crucible and evaporate the sulfuric acid fraction to near dryness. Cool and add 25 ml of concentrated HNO₃. Evaporate to near dryness. (one or two drops). Cool.
- Add 2.0 mg of La carrier. Then transfer with distilled H₂O to a 40 ml centrifuge tube.
- Dilute to approximately 30 ml with the distilled H₂O, and then add saturated NaOH until the pH reaches 12 and add a few drops in excess.
- Digest the precipitate at 95°C, then cool to room temperature. Centrifuge for 10 minutes.
- Decant and discard the supernatant liquid. Dissolve the precipitate with three or four drops of concentrated HClO₄ and wash down the sides of the C-tube using a minimum of distilled H₂O (less than 5 ml).
- Transfer to a 25 ml volumetric flask with less than 5 ml of distilled H₂O.

Colorimetric Procedures

CHROME AZUROL S PROCEDURE

- Add 2 drops of 1% p-nitrophenol.
- Add 5*N* NaOH until the yellow color just appears.
- Add 1*N* HClO₄ until the yellow color disappears permanently.
- Add one drop of concentrated HClO₄.
- Add one ml of a 10% solution of NH₂OH-HCl. Heat until solution just begins to boil.
- Cool slightly and add 10 ml of the buffer solution. Stir well.
- Add one ml of Chrome Azurol S dye, and stir. Adjust volume to 25 ml with H₂O and stir.
- Allow sample to stand for 10 minutes, then read the transmission on a Model DU Beck-

man Spectrophotometer at a wavelength of 610 millimicrons.

THORIN PROCEDURE

1. Add 10 drops of concentrated hydrochloric acid to the lanthanum hydroxide precipitate from step #21 in the Isolation Procedure.
2. Transfer the solution to a 25 ml volumetric flask. Dilute the sample with approximately 10-15 ml of distilled water.
3. Add two ml of 10% hydroxylamine hydrochloride, then one ml of 0.1% thorin solution.
4. Measure the absorbance at 545 millimicrons using a Model DU Beckman Spectrophotometer.

MORIN PROCEDURE

1. Add one ml of perchloric acid pH 1.0 to the lanthanum hydroxide precipitate from step #21 in the Isolation Procedure.
2. Add 10 ml of perchloric acid pH 2.0.
3. Heat centrifuge tube at 85-90°C until precipitate is dissolved. Cool solution to room temperature.
4. Add one ml of 10% hydroxylamine hydrochloride. (Perchloric acid, pH 2.0, is used as solvent.)
5. Add one ml of morin solution, then transfer solution to a 25 ml volumetric flask and dilute to volume with perchloric acid pH 2.0.
6. Measure the absorbance at 410 millimicrons using a Model DU Beckman Spectrophotometer.

Discussion

OXALATE PRECIPITATION

The oxalate precipitation of thorium described by Willard and Gordon⁷ and studied by Kall and Gordon¹¹ in the presence of calcium is essentially quantitative. This was confirmed by precipitation of ionium²³⁰ with varying amounts of calcium, 25-200 milligrams, from synthetic solutions. In all cases no detectable quantity of the added isotope was observed in the filtrate.

EXCHANGE OF THORIUM

Effect of Ion Exchange Resin Type: As previously stated, thorium is readily adsorbed by ion exchange resins. Therefore, it was considered the best approach to use a resin of a loose cross-linked network so that elution of the adsorbed thorium ion would not be too difficult. Dowex 50 X-4 (50-100 mesh) was selected as the resin suitable for this work. Experimentation showed

10% loss of thorium during the water wash and the 3N hydrochloric acid elution step. Dowex 50 X-8 (200-400 mesh) completely adsorbed the thorium from a 0.5N hydrochloric acid solution and retained thorium quantitatively during the water wash and the 3N hydrochloric acid elution step. This resin was used for the work reported in this paper.

Effect of Anions: In the presence of urine salts added thorium was not recovered in the 4M H₂SO₄ elution step. Thorium forms a number of complexes with sulfate and phosphate anions. These complexes range from neutral to a plus four charge accounting for the distribution of thorium throughout the waste, water wash, and the 3N hydrochloric solutions.

A double phosphate collection step improved the thorium recovery to 40% indicating that phosphate and sulfate were both complexing the added thorium. The inclusion of an oxalate precipitation, prior to introduction of the sample to the resin column, reduces the amount of phosphate and sulfate and enables the resin to adsorb the thorium ion in the plus four state.

CATION INTERFERENCE

The presence of calcium in the final solution to be analyzed for thorium content increased and shifted the absorbance. The ion exchange procedure removes quantitatively calcium, barium, and other ions that may precipitate as an oxalate. It also separates the thorium from trace interferences of iron and uranium that may be occluded by a single oxalate precipitation step.

ELUTION OF EXCHANGE THORIUM ION

Preliminary work had shown that thorium ion once adsorbed on the resin column was difficult to remove with normal concentrations of hydrochloric acid. Several methods have reported the elution of thorium from ion exchange resins with organic reagents by the formation of neutral or anionic complexes. (Citric acid, diammonium citrate, etc.) This approach was discarded because of the necessity of destroying large amounts of organic material before the spectrophotometric analysis could be performed. A survey of the mineral acids showed that concentrations of sulfuric acid above 2M have elution efficiency suitable for routine analysis.

COMPARISON OF COLORIMETRIC DYES

The existing spectrophotometric methods based on the dyes thorin, morin, and Chrome Azurol S are capable of detecting microgram quantities of thorium. These reagents are not

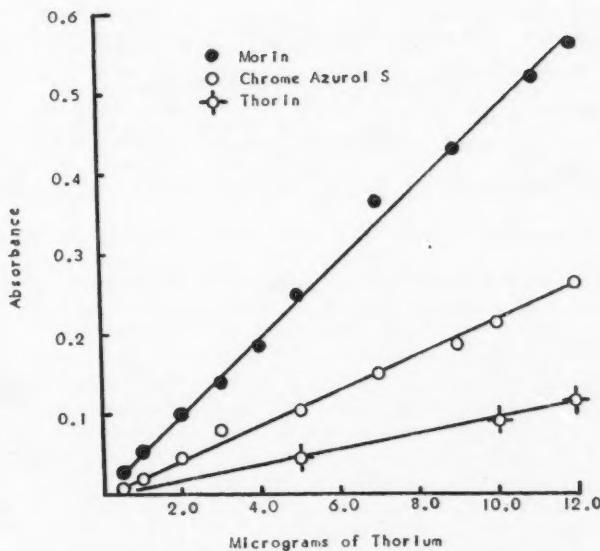


FIGURE 1. Analytical curves for thorium determination.

specific and react with various other metal ions. Applying the isolation procedure, previously described, these reagents have been used to determine added thorium from large volumes of urine.

Figure 1 presents the analytical curves for each dye at the specified wavelength:

Thorin—545 millimicrons

Morin—410 millimicrons

Chrome Azurol S—605 millimicrons.

The three reagents in decreasing order of their sensitivity are morin, Chrome Azurol S, and thorin. All of the reagents are subject to interference from sulfate, ferric ion, and aluminum. Ferric ion is eliminated by reduction to the ferrous state by the addition of hydroxylamine hydrochloride. Although the concentration of aluminum in urine is low, considerable quantities are picked up from glassware during evaporation procedures. All evaporation and ashing procedures should be carried out in platinum ware. The lanthanum hydroxide step is added to remove the last traces of aluminum. Most of the sulfate ion is removed during the evaporation in platinum. Care must be taken to avoid prolonged heating of the thorium which renders the ion relatively insoluble. The last traces of sulfate are removed by the lanthanum hydroxide precipitation.

RECOVERY OF ADDED THORIUM

Known amounts of thorium were added to one liter samples from personnel without any

TABLE I
Recovery of Thorium from Urine

Level of thorium added micrograms	Per cent thorium found		
	Chrome Azurol S	Thorin	Morin
1	92.0 ± 14.3	—	95.3 ± 15.3
3	86.6 ± 13.4	93.0 ± 9.3	90.6 ± 17.3
5	98.0 ± 11.5	100 ± 12.1	91.2 ± 13.6
10	101 ± 9.4	99.0 ± 7.2	97.3 ± 11.1
All levels	95.9 ± 12.2	98.6 ± 10.4	94.2 ± 15.6

history of thorium exposure. The thorium was added to the sample prior to the calcium phosphate precipitation step and carried through the isolation procedure as outlined. Table I summarizes the results obtained by the three dyes at 1, 3, 5, and 10 micrograms of added thorium. Each result represents an average of from five to ten separate analyses.

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A STYLE NOTE

BEGINNING in the February 1959 issue, A.I.H.A. Journal Vol. 20 No. 1, a small change in the style of the references in the bibliographies is being made. A single author or first author of several will be listed last name first followed by initials; other authors following in the reference will be identified by initials and last name in that order. This will eliminate the confusion of setting off in commas the initials of these authors, as well as the reversal of normal order which appears to serve no purpose. This reversal is retained for single or first authors for better appearance and for greater ease of finding a reference by name. See Information for Authors in this issue, page 18.

INFORMATION PLEASE

THE OCCUPATIONAL Health Information Exchange, U. S. Public Health Service, 1014 Broadway, Cincinnati 2, Ohio is seeking information on the production, uses, hazards, controls, and toxicities of the following materials:

2-propynyl sulfide
tetrachloro phthalic anhydride
diethylene triamine
carbonyl fluoride
propargyl amine
propargyl bromide.

Any information on these items or reference to other sources will be appreciated.

Sampling Effluent Gases for Particulate Matter

R. W. WASSE

Public Service Electric and Gas Company, Maplewood, New Jersey

THE PROBLEM of removing particulate matter from the effluent gases discharged to the atmosphere by central station boilers has greatly increased since the introduction of pulverized coal firing. Most utility companies have spent considerable sums of money to purchase and install dust collecting apparatus in order to reduce atmospheric contamination. It is also the practice of most of these companies to conduct tests on dust collectors when originally purchased, and periodically thereafter, to determine whether the collection efficiency meets the manufacturer's guarantee. This paper describes the test equipment and procedure used to obtain representative samples of such effluent gases and to determine the concentration of particulate matter therein. While the procedure outlined is particularly adapted to central station boilers, the same procedure, with minor modifications, may be used to determine the particulate matter in any confined gas stream.

Essentially, the test is conducted by passing a measured portion of the flue gas through a filtering device under carefully controlled conditions, and weighing the particulate matter retained by the filter. In sampling central station boilers, it is necessary to take samples at a number of points in a cross section of the gas stream in order to obtain an average value. Sampling stations are provided during the erection of the boiler in accordance with the ASME power test codes for *Dust Sampling Apparatus and Determining Dust Concentration in a Gas Stream*.

If the results are to be accurate, it is necessary that the velocity of the gas entering the sampling apparatus be equal to the velocity of the gas in the duct. The sampling apparatus must be designed so that the gas sampling rate may be accurately controlled. Essential parts of the sampling apparatus are:

- (a) A tube or nozzle for insertion into the gas stream to be sampled.
- (b) A filtering or separating device for removing the dust from the sampled gas.
- (c) A means for checking the approximate equality of the velocity of the gas entering the nozzle and the velocity of the gas in the flue at the point of withdrawing the sample.

(d) A meter for measuring the quantity of gas sampled.

(e) An exhausting device for drawing the gas through the nozzle, filter and meter.

A number of different types of sampling devices have been developed and successfully used. Figure 1 shows several representative types of sampling devices.

The sampling device used by the Testing Laboratory of the Public Service Electric and Gas Company contains the following parts:

(a) A balanced draft sampling nozzle made of stainless steel.

(b) An integral sampling head designed to receive a Norton Co. No. 9418 alundum extraction thimble. The head is made of 17-ST aluminum alloy.

(c) A length of one-inch pipe to which the sampling head is attached. The length of this pipe is dependent on the size of the duct being traversed. A moisture trap is built into this pipe at the end where it screws into the sampling head. Stainless steel tubes, used to transmit the static pressures at the balanced draft nozzle, enter the one-inch pipe above the moisture trap and extend the entire length of the pipe.

(d) An inclined differential draft gage with the zero at the center of the scale is used for regulating the flow of sample.

(e) A No. 1 Emco test gas meter is used for measuring the quantity of gas sampled.

(f) A Schutte and Koerting steam jet exhauster is used for drawing the gas through the sampling nozzle, alundum thimble, pipe, and meter.

(g) Miscellaneous equipment—rubber tubing, hose clamps, manometer, engraved stem thermometer, etc.

Figure 2 shows an assembly of the parts that make up this sampling device. The data for ordering the equipment are given in Table I.

Figure 3 shows an exploded view of the integral sampling head and a balanced draft sampling nozzle.

Figure 4 is a drawing of the balanced draft sampling nozzle. This is a modification of the Pitot tube developed by Prandtl.¹

The original tests are usually conducted after

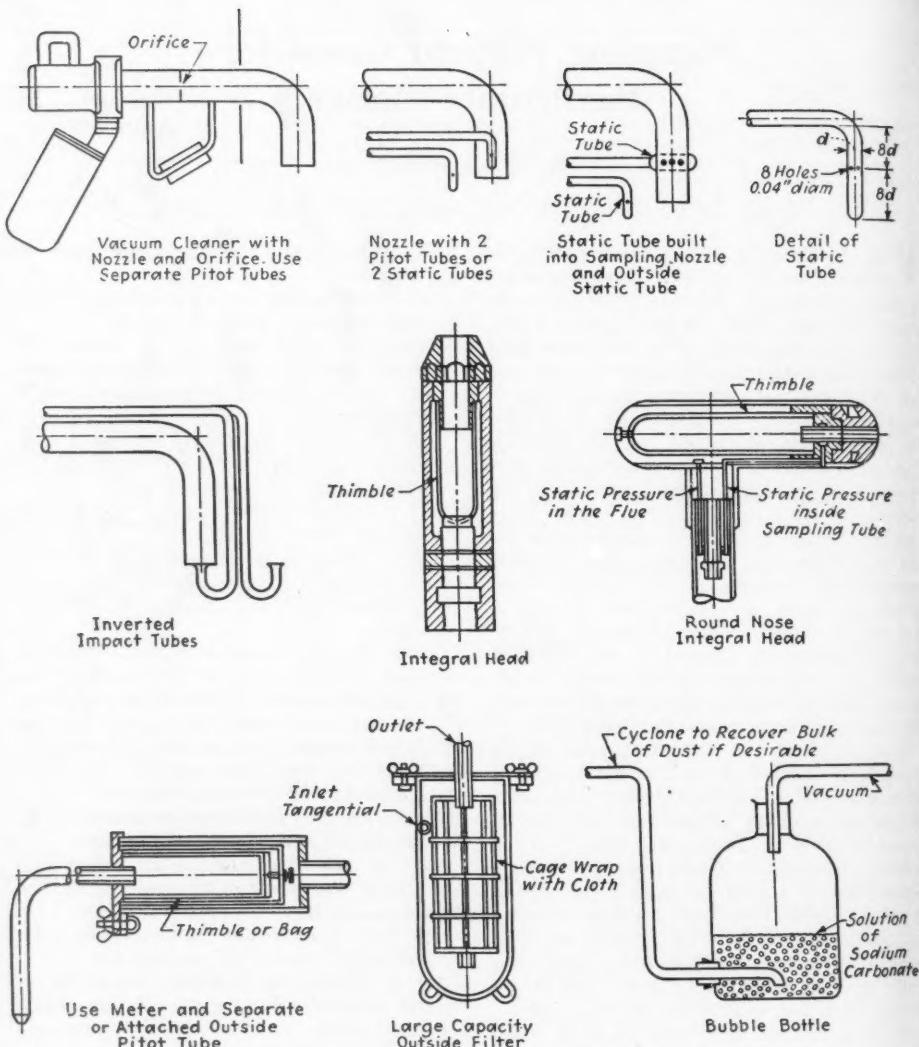


FIGURE 1. Sampling devices. (ASME Power Test Code, 27-1957.)

the manufacturer's representatives have made the necessary adjustments to the collector and consider its performance satisfactory. At this time complete velocity, temperature, and gas analysis traverses are made of each of the sampling stations. From these traverses, the various sampling points are established.

After the sampling points have been established, the sampling devices are installed. During this period other equipment is checked and readied. The thimbles are inspected for defects

such as cracks or nicks, extraneous matter is removed, and they are numbered on the side and bottom. The thimbles are then dried in a drying oven at 250°F for a minimum of two hours after which they are cooled in a desiccator and weighed to the nearest 0.1 mg. Following this they are stored in individual screw-top jars until needed. For convenience special racks which fit both the desiccator and the drying oven are provided to hold the thimbles. Double numbering permits identification of the thimble during

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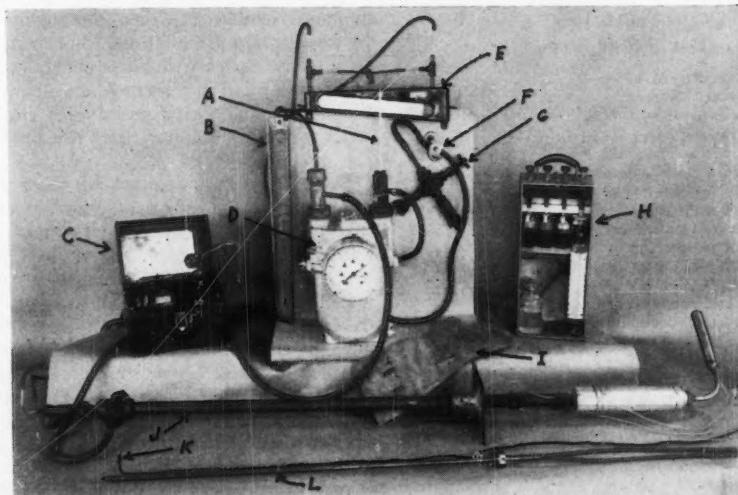


FIGURE 2. Test equipment: A. Thermometer, B. Monometer, C. Potentiometer, D. Gas meter, E. Draft gauge, F. Regulating clamp, G. Aspirator, H. Orsat, I. Asbestos mitt, J. Assembled dust probe, K. Thermocouple, L. Pitot tube.

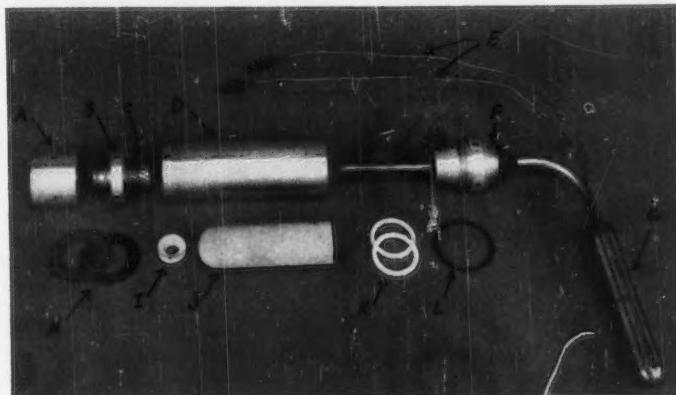


FIGURE 3. Exploded view of sampling head: A. Coupling, B. Lock nut, C. Thimble tightening sleeve, D. Body, E. Static pressure leads, F. Nose, G. Sampling nozzle, H. Hard asbestos lock nut gaskets, I. Teflon gasket, J. Alundum extraction thimble, K. Soft asbestos thimble gaskets, L. Hard asbestos nose gasket.

weighing or when positioned in the sampling head.

For the test a dust probe and gas meter with the auxiliary equipment are used at each sampling station.

Before each test run, the dust sampling equipment is subjected to a leakage test. This is done by assembling the equipment, plugging the open end of the sampling nozzle and applying a suction to the complete assembly. If the pointer

on the gas meter does not move after the initial evacuation, the equipment is considered tight and is ready to be inserted in the gas duct. A tag with the station and thimble number is placed on the meter. After the leakage tests have been made, the probes are inserted in the duct to the furthermost sampling point with the nozzles pointing down-stream. The reason for starting with the maximum probe length in the hot gas stream is that at the end of the traverse a

TABLE I
List of Equipment

Ellison inclined draft gage 0.5"-0-0.5"
Ellison draft gage oil 0.834 sp. gr.
20" U-tube glass manometer
Mercury for manometer
Jumbo "Castaloy" hose cock, SGA #C4875
Schutte & Koerting steam jet exhauster, $\frac{3}{4}$ " bronze
Rockwell EMCO No. 1 gas meter
Engraved-stem glass thermometer—3" immersion 0-220°F range
Ellison 50ML portable gas analyzer, 3 chambers
Stauwcheibe Pitot tube equipped with an I.C. thermocouple
L&N direct-reading I.C. potentiometer
Asbestos mitts
Dust sampling probe equipped with balanced draft head
Assorted gaskets and Teflon insert for dust sampling probe
Thimbles:
Whatman paper extraction 33 x 94 mm single thickness
"No. 6406 porosity R.A. 98 30 x 80 mm
No. 9418 porosity R.A. 98 45 x 150 mm
Assorted sizes of heavy wall rubber tubing
Rubber tubing clamps

larger portion of the probe is cool, which makes handling easier. At a predetermined time all nozzles are pointed up-stream, the gas flow is started and regulated to maintain a zero reading on the draft gage. Usually the pointers on the gas meters are set at zero before the start of each test. Gas flow, meter suction and temperature are read and recorded at five-minute intervals for the entire test run. The duration of a run may be up to four hours and every effort is made that, during this period, the conditions remain steady.

The length of time that the gas is sampled at a given point is determined by the total duration of the test run and the number of points at a sampling station.

At the end of the test run the gas flow is stopped and the sampling nozzles are simultaneously pointed down-stream. The probes are then removed from the duct. The head is disconnected, tapped in such a manner that all the particulate matter that is lodged in the sampling nozzle falls into the thimble. Great care must be taken at all times in handling the probe and head to prevent damaging the thimble or spilling the sample. The thimble is again placed in a screw-top jar for transporting it to the laboratory. At the laboratory the thimbles are dried, cooled and weighed in the same manner as before the test. At times when the weighing bottle is cleaned by brushing, an electrostatic charge will be introduced that will cause an error in weighing. It is, therefore, advisable to remove the debris from the weighing bottle by inverting and tapping the bottle gently against the table surface. After weighing, the fly ash is removed from the thimble for chemical and size analyses. The

alundum thimbles are then thoroughly cleaned by soaking in a 5% solution of hot nitric acid for four hours, rinsed with clear water, soaked in a 5% solution of hot ammonium hydroxide for four hours and again rinsed with clear water. After drying in an oven they are prepared for the next test.

Several precautions must be taken during a test to offset the effects of excessive condensation especially during cold weather. All lines should slope away from the probes, and only probes with built-in standpipes of sufficient height to prevent any liquid to drain back on the thimble should be used. Any overflow of liquid into an alundum thimble will only cake the sample, but when paper thimbles are used they will rupture and the work will be a total loss. A standpipe built into the sampling head as an extension of the sampling nozzle and reaching about halfway into the thimble will lessen the chance of spilling the sample during the handling of the probe at the end of the test run. It should be made certain that there is no moisture from the previous test left anywhere in the dust sampling equipment.

Dust concentration computations may be made very simple by dividing the dust weight by the corresponding gas volume as registered by the meter, corrected for meter accuracy and to standard temperature and pressure. They may be made considerably more complex by using every refinement such as the moisture content and chemical analysis of the flue gases to obtain the mass per mass concentration. The choice of method depends entirely on the purpose of the test. Very often too many refinements in computations are not necessary as they cancel out to a certain extent and the precision of the test does not warrant the additional labor.

The development of the present method of sampling covers a number of years of testing dust separating apparatus. Initially the laboratory used to make a Pitot tube traverse of the inlet and outlet ducts. The velocities determined from these traverses were used to establish the withdrawing rate at the meter. From this it was assumed that the velocity in the sampling nozzle would be the same as the velocity of the gas in the main stream at the point of sampling. This, however, was quite often not the case. When the withdrawal rates were calculated, consideration had to be given to the temperature and pressure differences between the gas in the duct and the gas at the meter. During a test, temperature changes took place both in the duct and at the meter. The pressures at the meters were changing as the filters became clogged with dust. Finally there was also the fallacy in the

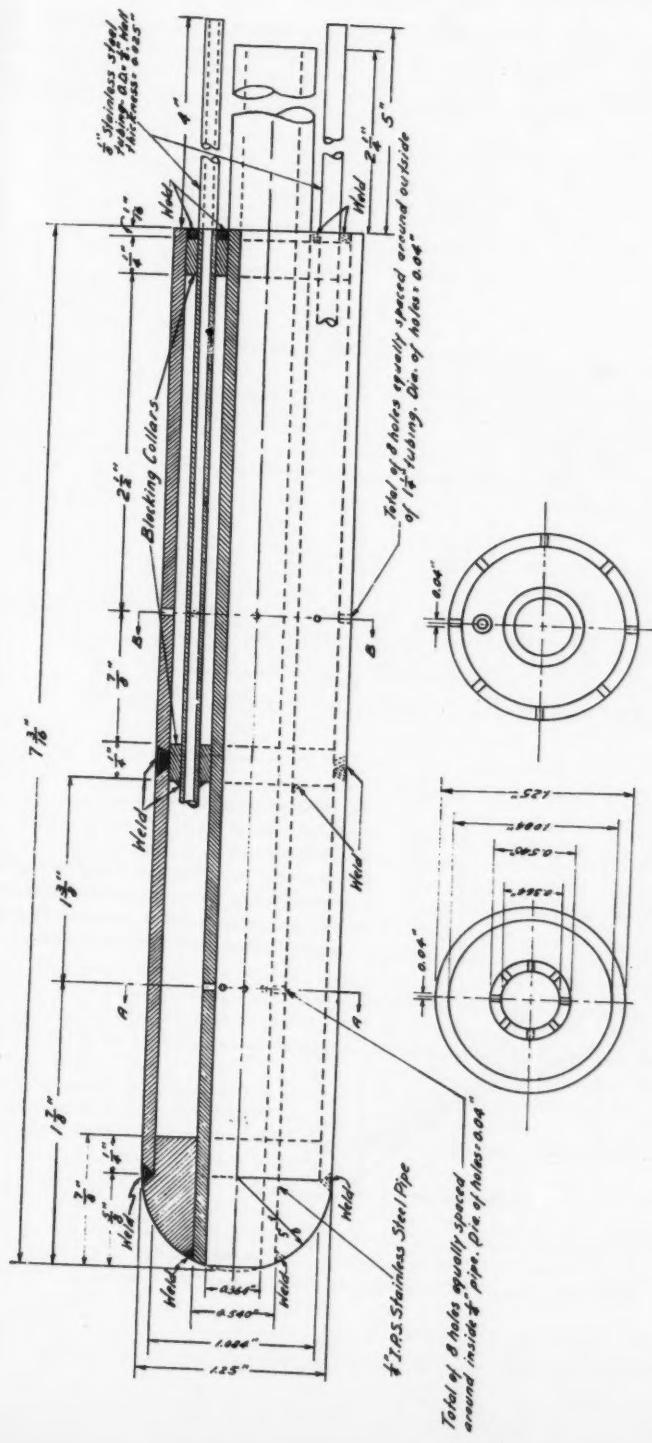


FIGURE 4. Construction drawing of balanced draft sampling nozzle.
Section A-A *Section B-B*

assumption that during the entire test period, which may have lasted several hours, the gas flow pattern had not changed.

In order to demonstrate the effect of having

improper sampling rates Figure 5 is presented. If the sampling velocity (V_s) is greater than the duct velocity (V_d), the heavier particles that were entrained in the outer portion of the with-

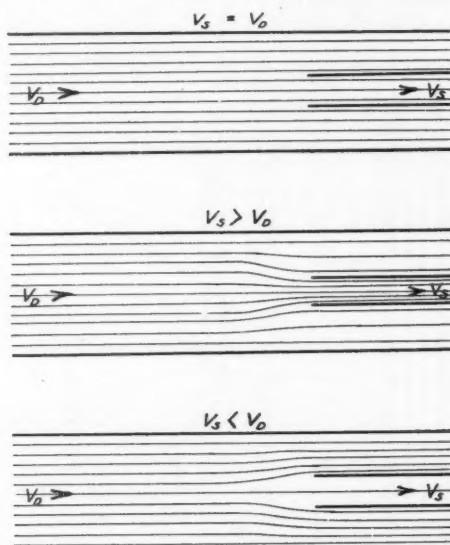


FIGURE 5. Duct velocity (V_d) vs sampling velocity (V_s).

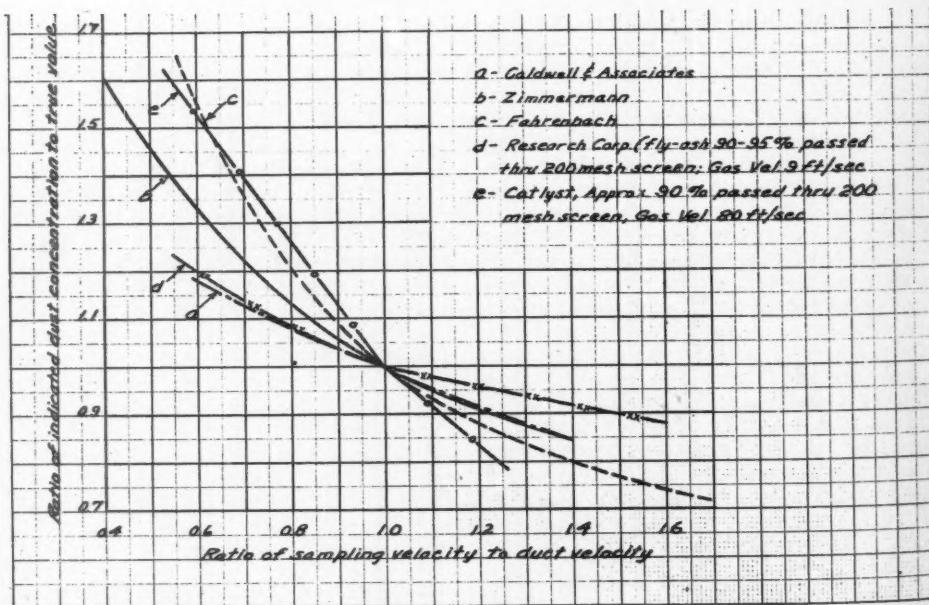


FIGURE 6. Effect of withdrawing rate on indicated dust concentration.

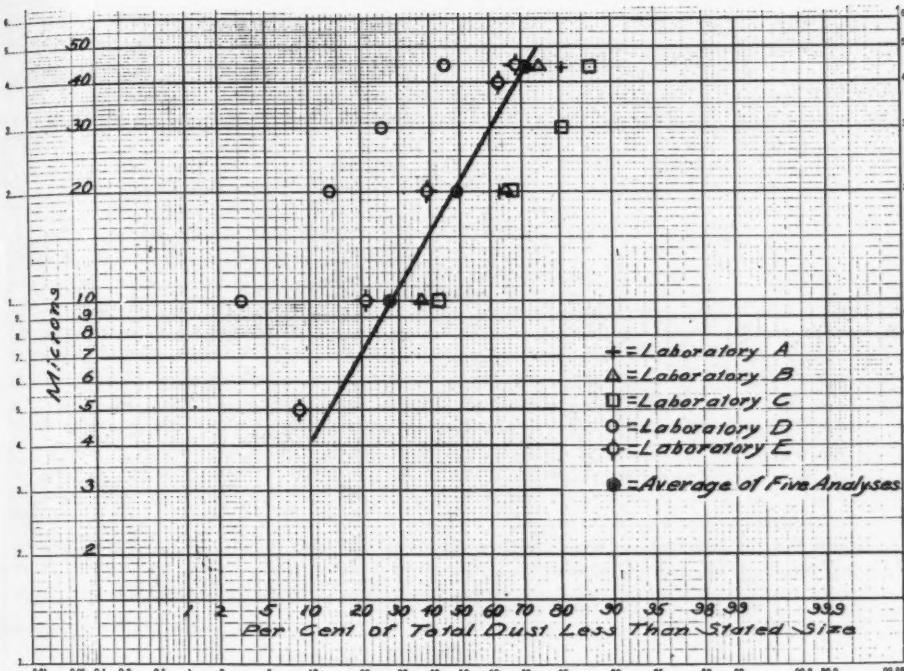


FIGURE 7. Flue dust subsieve size analyses by various laboratories.

drawn gas will by-pass the sampling nozzle. On the other hand, if $V_s < V_d$, the outer gas strata by-passes the sampling nozzles but the inertia of the heavier particles will cause them to enter the sampling nozzle. The results of the deviations of the ratio of the sampling velocity to duct velocity from unity as obtained by various investigators^{2, 3, 4} is shown in Figure 6. The variation of the slopes of the different curves can be understood if we keep in mind that the error due to the wrong sampling rate is a function of the particle mass and the square of the particle velocity.

There are considerable variations in the size, shape, and density of fly ash particles. Flue dust particles are mostly perfect cenospheres of silica, aluminum oxides and iron oxides. Their size distribution is shown in Figure 7. The analyses show the difficulty in obtaining reproducible results in subsieve size analyses of the same sample based on the same physical law and done by nationally known organizations.

It is imperative that the concentration of the gas sample be the same as the concentration in the main gas stream. This is obtained by regu-

lating the nozzle velocity to equal the duct velocity. In order to have the velocities equal, the balanced draft sampling nozzle now used was developed.

The balanced draft sampling nozzle affords a more exact and simpler method of isokinetic sampling. The underlying principle of this nozzle is that when the velocity of the gas in the nozzle is the same as the velocity of the gas in the duct the static pressure of the gas flowing in the nozzle is the same as the static pressure of the gas flowing in the duct at the point of sampling. For test purposes it is only necessary to keep the flow of sample at such a rate that the inclined differential draft gage connected to the two static pressure connections reads zero.

Acknowledgments

The author wishes to express his appreciation to the American Society of Mechanical Engineers and to Research-Cottrell Inc. for their permission to use some material from their publications. Also particular acknowledgement is made to Mr. Edwin P. Norwood, Mechanical

December, 1958

Division Chief of the Testing Laboratory for his assistance in the preparation of this paper.

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BRITISH OCCUPATIONAL HYGIENE SOCIETY

A NNALS OF OCCUPATIONAL HYGIENE is the name of the new journal which will be the official organ of the British Occupational Hygiene Society. To be published as a quarterly, this journal will contain papers both of a practical nature and in the fundamental sciences relating to occupational health. It is anticipated that some 25 per cent of the articles will be of a clinical nature and the others will include engineering, statistics, physiology, chemistry, physics, fluid mechanics, pharmacology, etc.

Members of the Society will receive the journal automatically and without charge. Other individuals may subscribe for £2 s12 d6. (Libraries, industrial concerns, and governmental agencies £3 s10 d0, with special quotation for orders of three or more copies.) Address subscriptions or inquiries to Pergamon Press Ltd., Pergamon House, 4, Fitzroy Square, London, W.1, England.

RADIATION HYGIENE MEASUREMENTS

THE INSTITUTE of Industrial Medicine and the College of Engineering of New York University with the assistance of the U. S. Atomic Energy Commission are offering a course in Radiation Hygiene Measurements May 4 through 29, 1959. This is a laboratory course for persons having some knowledge of nuclear measurement principles and required to deal with specialized radiation protection problems. The experiments will include work with neutron sources, mixed radiation fields, and the shielding of various radiation sources. Principles of scintillation pulse height analysis, nuclear track microscopy, statistics of nuclear counting, and electronic principles of nuclear detection equipment will be treated.

For applications and information write to Office of Associate Dean, New York University, Post-Graduate Medical School, 550 First Avenue, New York 16, New York.

Calibration of Alnor Velometers

GEORGE M. HAMA

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THE Alnor Velometer* is a direct reading velocity meter which because of its portability, instantaneous reading feature, wide velocity range, ease of making measurements and its ability to measure air flow at hood and duct openings has found large usage as a field instrument. The instrument must, however, be calibrated to give accurate results. To assume that an uncalibrated instrument will give accurate values after several years of usage will result in measurements grossly in error. Tables I and II give the comparison of true velocity and velometer readings for 11 velometers.

It is the purpose of this paper to outline calibration methods for the Alnor Velometer as an air velocity meter for determining velocity (fpm) into exhaust hood and duct openings.

Accuracy of the Instrument

Velocity measurements made at duct, hood, and booth exhaust openings are inherently inaccurate as compared with measurements made within the duct some distance from bends, openings and branch entries. This is because most hood and duct openings have high entry losses with non-uniform, turbulent, and erratic air flow. Tables III, IV and VI illustrate this non-uniform air flow.

Also, the Alnor Velometer has certain characteristics¹ which limit its accuracy. These are:

1. The short length and compression of the scale in certain ranges reduce the precision of the reading.
2. The fluctuation of the pointer during a velocity measurement limits the certainty of the exact point to be read.

A linear error of 0.02 inch in reading this scale must be allowed. At 400 fpm (on certain velometers) this represents about 25 fpm or over 6% of the actual value.

It is doubtful if readings with the Velometer over all ranges can be made closer than within a $\pm 5\%$ error—even under laboratory conditions.

In field measurements unless a careful and multiple point traverse is made at the exhaust opening, the error may be considerably greater. If a single reading is made at an exhaust open-

ing, the error may be as great as 50 to 100%. This is illustrated in Tables III, IV and VI.²

Frequency of Calibration

All new instruments should be calibrated before being put into field use. Any instrument that has been dropped or subjected to contaminated and corrosive atmospheres should be recalibrated. A small flow of air takes place through the Velometer—corrosive gases will therefore get into the instrument.

An instrument that does not zero properly should be recalibrated. A zero check can be made by holding the Velometer in a steady vertical position and closing both ports. If properly at zero, the pointer will rest at the left end of the scale. Before calibration, the zero should be checked and adjusted to the left end of the scale by the center adjusting screw. Instruments in constant field use should be calibrated at least every year.

Unreliable Methods of Calibration

Because there is a tendency to believe that a quick reliable check can be made at any opening where the air flow is known, it is believed necessary to say a word on unreliable methods. Calibration of velometers should not be made at plain duct, hood, or booth exhaust openings.

These openings have non-uniform air flow with a high velocity *vena contracta*³ or vortex.⁴

This has also been confirmed by other investigators. Silverman⁵ states regarding a study of center line velocities into 2- to 20-inch diameter plain duct openings, "Velocity at the openings and near the openings is from 1.5 to 2 times the average velocity in all cases. The measurement of velocity close to the mouth within $\frac{1}{2}$ inch gave erratic results because of turbulence. . . . The increased velocity at the face is due to the formation of a vortex at the edges of the pipe mouth by air brought in from behind the openings."

Also a change in the position of the jet in and out of the duct in line with the air flow will cause large changes in velocity. This is illustrated in the results shown in Table VI.

It is believed that even if the calibration is made by a careful multiple point traverse at

* Trade name of Illinois Testing Laboratories, Inc., 420 North LaSalle Street, Chicago 10, Illinois.

TABLE I
Calibration Data on 11 Velometers
Comparison between actual velocity (fpm) and
velometer reading (fpm) using the
0-2500 fpm exhaust, jet

Velometer No.	Actual velocity true fpm	Velometer reading fpm
1	2060	1450
2	1980	1600
3	1860	1875
4	2260	2360
5	2260	1875
6	2260	1350
7	1860	1072
8	2260	1330
9	2380	1560
10	1190	1070
11	2260	1340

TABLE II
Calibration Data on 11 Velometers
Comparison between actual velocity (fpm) and
velometer reading (fpm) on low
velocity scale—no jets

Velometer No.	Actual velocity true fpm	Velometer reading fpm
1	166	230
2	166	215
3	116	222
4	107	135
5	166	157
6	125	126
7	118	118
8	118	118
9	192	191
10	144	143
11	192	201

plain duct openings and compared with the actual air flow from an accurate metering device, the results will result in a calibration error because the air stream does not fill the duct and portions of the stream are highly turbulent.

Under no circumstances should a Velometer exhaust jet be used for measuring flow or calibration by placing the exhaust jet within duct downstream from the exhaust opening. The static pressure within the duct will partially convert into velocity pressure in the Velometer and produce a reading tremendously in error.

Recommended Calibration Methods

The Velometer exhaust jets and low velocity gauge without jets should be calibrated in an airstream which is uniform, predictable and free

from turbulence. These conditions can be obtained from a streamlined or bell-shaped approach of large reduction area. A calibration system of this type is shown in Figure 1.

A simple satisfactory streamline bell-shaped approach can be made by following an elliptical curve. A satisfactory elliptical calibration entry can be constructed by the following dimensions:⁴

- a = semi-major axis
- b = semi-minor axis
- d = duct diameter connected to the elliptical approach
- a = d
- b = $2/3d$.

The bell-shaped approach must be smooth and free from irregularities. It must be exactly tangent to the duct. The precise curvature is not as important as smoothness of the curve.

The streamline approach used by the writer for jet calibration was constructed from a Sousaphone Horn smoothly soldered and connected to a 6-inch diameter round duct. This approach had excellent characteristics. It had an extremely low entry loss of 2% velocity pressure. (A plain duct opening has an entry loss of approximately 97% velocity pressure.⁵) The air flow across the diameter was uniform from the extreme edges to the center as shown in Table III. The velocity was uniform in line with flow from the entrance of the duct to five inches inside the duct (see Table VI).

A large diameter bell entry for low velocities (at least three square feet in area) is difficult to construct. The writer found a satisfactory but not perfect streamline calibration entry for the Velometer low velocity scale could be constructed from an approximately three square feet rectangular opening with curved air foil sides (see Figure 2). The uniformity of this entry can be illustrated by the velocity pattern shown on Table V.

An accurate metering arrangement is necessary for determining the actual velocity in the calibration system. An orifice meter, Venturi

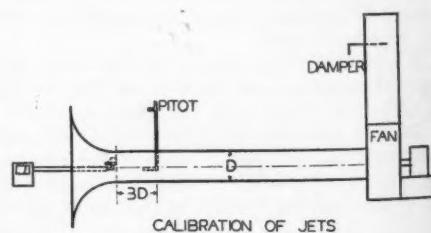


FIGURE 1

TABLE III

Air Flow Pattern Across the Diameter of Streamline and Plain Duct Openings for 6-Inch Diameter Duct

Distance from edge inches	Streamline opening velocity fpm	Plain duct opening velocity fpm
1/8	1500	1720
1/2	1490	1470
3/8	1490	1325
1 1/8	1490	1200
2	1490	1225
Center	1500	1170
2	1500	1100
1 1/8	1490	1150
3/8	1490	1650
1/2	1490	1750
7/8	1490	1800

TABLE IV

Center Line Velocity Expressed as Per Cent Average Velocity

Plain duct openings 6-inch to 20-inch diameter

Diameter inches	Centerline velocity expressed as % average velocity at opening
20	178
16	152
12	115
10	100
8	90
6	82

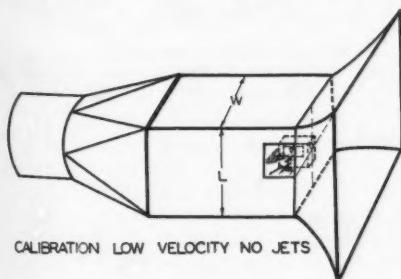


FIGURE 2

meter or standard Pitot tube can be used. The writer used a standard Pitot tube with an inclined manometer as the other metering devices were not available. The inclined manometer was graduated with .005-inch divisions and was calibrated against a Hook gauge.⁸ Two ten-point traverses were made across the 6-inch diameter duct (see Figure 1) at right angles to each other to determine the average velocity. A fixture was used to keep the Pitot tube at right angles to

the air stream. With a streamline entry calibration system it is not necessary to locate the Pitot tube metering point 7½ diameters downstream from the opening as it is done in fan testing as the air flow is more uniform close to the bell. Care must be taken, however, that the Pitot tube is not located so close to the jet being calibrated that the air stream is disturbed at the Pitot tube. Straighteners should be used before the Pitot tube, if the air stream is "cork screwed" or helical. This can be ascertained by observing the pattern of the air stream in the duct with small pieces of paper and smoke.

The Pitot tube needs no calibration and will give fairly precise readings in velocities above 1200 fpm. It is assumed that the manometer can be read to at least $\pm .005$ inch water gauge.

TABLE V
Air Flow Pattern on Streamline Rectangular Opening
25 Point traverse
velocity in feet per minute

+200	+190	+190	+190	+185
+195	+195	+195	+195	+190
+195	+190	+195	+185	+190
+190	+190	+190	+185	+195
+185	+190	+190	+195	+195

Average fpm 191

TABLE VI
Velocity Variation in Line of Flow
Stream line entry vs plain duct opening

Distance in duct from opening inches	Streamline opening velocity fpm	Plain duct opening velocity fpm
5	1490	—
4	1490	1650
3	1490	1650
2	1490	1600
1	1490	1350
0	1490	1170
1/2 Out	—	970

TABLE VII
Accuracy of Pitot Tube If Read to $\pm .005$ Inch Water Gauge

Velocity pressure in. H ₂ O	Velocity fpm	Range of deviation %
.062 $\pm .005$	1000 ± 40	$\pm 4.0\%$
.249 $\pm .005$	2000 ± 20	$\pm 1.0\%$
.561 $\pm .005$	3000 ± 10	$\pm 0.3\%$
.998 $\pm .005$	4000 ± 10	$\pm 0.25\%$

Table VII gives the $\% \pm$ error for several velocity ranges.

In calibrating the Velometer with exhaust jets and without jets (meter only), it is important that the device is held or suspended with a rod or other arrangement with a small enough area so it does not block the air stream or cause turbulence at the point of calibration. The velometer or jets should not be held with the hands.

The blocking area of the exhaust jet is 0.48 square inches. In a calibrating duct section of 6-inch diameter or larger it will not appreciably block the air stream so that a higher velocity will result. The blocking area of the Velometer meter box alone with no jet is 12.95 square inches. An area of calibration ($W \times L$ in Figure 2) of 3 square feet or larger will not appreciably block the air stream. The meter box without jets should be suspended in the calibrating section so that the left hand port is flush with outer edge of the rectangular section adjoining the air foil or streamline sides. The section should be checked for uniformity by making a 30- or 40-point traverse in equal areas. If it shows some variance or some lack of uniformity, a multiple point traverse should be made at each calibration.

If the density of air varies appreciably from standard air (.075 lb/ft³—dry air at 70°F and 29.92 inches Hg barometer) corrections should be made both for the Pitot tube readings and the Velometer calibration. The calibration factor⁵ is inversely proportional to the square root of the density of the air being measured. The density⁵ varies about 4–5% with each 30° temperature change and about 3–4% with 1000 feet

change in altitude. Corrections should be made where changes of 5% or more in density occur.

The air flow can be varied for calibrating at several velocities by a damper on the discharge of the fan or a variable speed motor. The writer used both the damper and a variable voltage transformer for changing the motor speed. During a calibration traverse it is important to check the fan rpm with a direct reading tachometer—to make certain there is no change in fan speed and velocity. If the motor speed varies because of a fluctuating line voltage, a constant voltage transformer should be used. The calibration should be made against a number of velocities so a calibration curve can be plotted in the range in which the velometer is used.

Acknowledgment

The writer is indebted to Mr. R. McLean and Mr. Lawrence Curley of the Detroit Bureau of Industrial Hygiene for their able assistance in the calibration work discussed in this paper.

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Evaluation and Control of Lead Exposures in Powder Metallurgy Operations

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THE ASSOCIATION of lead exposure with powder metallurgy operations has received little attention in industrial hygiene literature. The study presented herewith substantiates the possibility of the existence of such exposure. Application of industrial hygiene methods to evaluate and control high atmospheric concentrations resulted in the elimination of a condition which might otherwise have produced cases of intoxication. The main factor in this particular hazard was recirculation of air containing excessive amounts of lead dust.

A plant engaged in the production of sintered powdered metal products was originally operated without the benefit of a medical and industrial hygiene program. Operations were carried out in a one story brick and steel building approximately 80 x 200 feet in size. The principal raw materials used were copper, iron, lead, tin, graphite and powdered silica. With regard to the lead employed, it should be noted that some of the metal powder mixes do not contain any of this element or its compounds while in others it may be present in the proportion of from 3 to 6 per cent. As the name of the process suggests the lead used is the metallic form but of an extremely fine particle size.

Under the present new management no essential change has occurred in the manufacturing process, the first steps of which are the weighing, mixing, and blending of the metal powders. The latter are then placed in presses having capacities of from 1500 to 2000 tons to evolve the shapes and sizes of the finished products. In this stage the resultant pieces or "compacts" as they are called, require sintering in electric furnaces before they are ready for the final operations of machining, grinding, buffing, inspecting, and shipping.

In November 1956 a complete medical and industrial hygiene program was set up for this plant which now employs from 125 to 150 workers on a three shift basis. Among other services the plan provides for urine and blood analyses which are correlated with results of air samples obtained at the breathing level in the working areas. In this way it is possible to

evaluate the degree of lead absorption among the employees with a reasonable degree of accuracy. The analyses are all performed by the same technicians in the hygiene laboratory of the medical department and are carefully checked through well established standards and techniques developed over the past 15 years.

In the first period of investigation samples of urine were collected from 122 employees in order to determine each individual's urinary lead output. No particular effort was made to classify these employees as to specific jobs or the areas of the plant in which they worked. Rather the survey presented an attempt to obtain a general idea of exposure to lead in the working environment as well as the number of employees who might show evidence of significant absorption. Based on our own experience as well as that of other investigators we consider urinary excretion values below 200 micrograms of lead per liter of urine to be within the normal range for workers exposed in this particular type of occupation. The mean excretion rate for the entire group of 122 employees was 99 micrograms of lead per liter of urine with 14 of these showing rates over 200 micrograms of lead per liter of urine and five of the 14 employees having values over 300 micrograms while two others had over 400 micrograms of lead per liter of urine. The range of values for these 14 workers was 225 to 471 micrograms of lead per liter of urine with an average of 300 micrograms. Accordingly these employees showing amounts of lead in their urines compatible with high lead absorption and the operations with which they were associated, were selected for special consideration in the proposed study.

To estimate properly the extent of the hazard and correlate atmospheric concentrations of lead with the urine findings, an industrial hygiene survey was conducted at the plant in March 1957. The results of this study demonstrated adequate amounts of lead in the air to produce the conditions observed in the workmen the previous November when the urine samples were obtained. Nineteen air samples collected with electrostatic precipitators over 30-minute

periods and analyzed for lead disclosed a mean of 0.26 milligram of lead per cubic meter of air and a range of 0.06 to 0.90 milligram of lead per cubic meter of air. As presented in Table II sixteen samples out of the 19 collected gave values of over 0.10 milligram of lead per cubic meter of air and of these sixteen, 10 samples were over 0.15 milligram of lead, the suggested maximal acceptable concentration then in use. (The American Conference of Governmental Industrial Hygienists has recently suggested a threshold limit value of 0.2 milligrams of lead per cubic meter of air.)

Machines were exhausted by local exhaust hoods connected to unit type collectors. (Figure 1.) The collectors were of the cabinet cloth filter type in which the dust laden air is drawn into the cabinet, through a set of cloth filters, through the fan chamber, and then back into the room via an exhaust vent on top of the cabinet. A tray located beneath the filters caught the heavier particles while the finer dust was drawn into the filters. The filters were cleaned by manual shaking and brushing and it was necessary to empty the collectors frequently.

The survey disclosed a number of conditions in the plant which contributed to some extent to the general pollution of the atmosphere but the high concentrations (0.70 milligram of lead per cubic meter of air in some instances) found in the discharge stream of the collectors from the presses left little doubt that the recirculated air was the most important source of contamination.

Improper hygienic and safety practices such as dry sweeping and the indiscriminate use of air hoses to clean off machines and cloth-

ing, added their share of dust to the general atmosphere and allowed particles to settle on the super-structure of the plant. It was obvious, therefore, that the conditions existing in the working areas were compatible with the creation of a definite lead hazard.

In addition to the evidence of lead exposure and absorption provided by analysis of the urine specimens and atmospheric samples, examination of the blood on eight of the 14 employees in the study confirmed in a lesser degree the potential danger of plumbism. Polarographic analysis of blood samples on these individuals gave an average concentration of 71 micrograms per 100 grams of whole blood. These results were within the upper limits of normal and though not indicative of impending intoxication, they did presage a possible trend toward seriously high lead absorption. It should also be remembered that the blood analyses were done in the month of September 1957 when the weather was warm and ventilation in the plant considerably better than in March or November when the air and urine samples were obtained; factors which could well have accounted for the lower amounts of lead observed in the blood. It has been our experience that good correlation between blood, urine, and air findings exists if the samples are collected at the same time when plant operating conditions are more uniform. By the same reasoning it might be stated that had the blood specimens been collected in March or November they would have shown greater than normal values for lead. Physical examination did not reveal any clinical signs or symptoms of illness due to lead in any of these eight employees. Regardless of this fact it was felt that the situation was fraught with serious possibilities and immediate steps for improvement should be taken.

Plans for an entirely new system of ventilation were adopted. Actually three separate systems were designed, each with a capacity to move 12,000 cubic feet of air per minute (cfm). The exhaust systems were connected to fabric collectors located outside the plant with no recirculation. Vacuum cleaning was substituted for dry sweeping and an educational program was introduced to secure employees' cooperation in maintaining good housekeeping and eliminating improper and unhealthful practices. Adequate volumes of tempered make-up air were assured by providing for this in the design of the new ventilation equipment.

Subsequent to the original collection of samples in November 1956 additional specimens of urine were collected each month from the 14



FIGURE 1. Recirculating type of unit collector.

employees who displayed elevated levels of urinary lead excretion. Lead-in-urine levels remained high through the winter and spring months, ranging from 300 to 400 micrograms of lead per liter of urine in some instances. During the warmer weather all employees showed decreased lead excretion rates but following the installation of the exhaust equipment, completed by October 1957, there was no increase in the urinary excretion rates with the cold weather season. The consistent and drastic reduction in urinary lead levels below those of the previous winter months demonstrates the efficiency of the corrective measures adopted.

The following tabulation (Table I) demonstrates the effect of reducing exposure to lead on the 14 employees participating in the study. The months of November 1956 and 1957 were selected from the other monthly sampling periods because the first survey was made in November 1956.

As shown by the table, seven samples of the 14 with lead-in-urine values of over 200 micrograms were found to be in the range of 300 to 471 micrograms in November 1956. In marked contrast, results of urine analyses for lead in November 1957, after the lead exposure had been controlled, showed the range to be 25 to 235 milligrams with only one employee's urine containing more than 200 micrograms of lead per liter. Furthermore, only three of the group showed values above 100 micrograms per liter of urine. The mean lead excretion for this entire group was 82 micrograms of lead per liter of urine, lower than the mean for the entire plant personnel in November 1956.

To correlate these improved results with the lead control measures instituted, another industrial hygiene survey was made at the same time the urine samples were collected in November 1957. The results of air samples, taken in the areas where the employees under consideration worked, are compared in Table II with those found in the survey of March 1957. These comparative values demonstrate the reduction

TABLE I
Urinary Lead Excretion Rates*—14 Employees

Month and Year	Total number of samples	Range	Mean	Number of samples		
				Over 200	Over 300	Over 400
November, 1956	14	225-471	311	14	5	2
November, 1957	12	25-235	82	1	0	0

* Expressed in micrograms (gamma) lead per liter of urine.

TABLE II
Concentrations of Lead-in-Air

Month and Year	Total number of samples	Range—mg/m ³	Mean mg/m ³	Number of samples above MAC	Number of samples above 0.10 mg/m ³
March, 1957	19	.06-.90	.26	10	16
November, 1957	12	.04-.15	.06	0	1

in atmospheric contamination attained by the substitution of the unit type collectors with their recirculation of air by collectors exhausting directly to the outside air and adoption of other control measures.

As indicated, none of the 12 air samples collected in November 1957 were above the maximal acceptable concentration of 0.15 milligram of lead per cubic meter of air as opposed to 10 samples above the allowable limit in March 1957. The drastic lowering of the mean lead-in-air concentrations from 0.26 milligram in March 1957 to 0.06 milligram of lead per cubic meter of air in November 1957 afforded conclusive evidence that the hazard had been adequately corrected.

Discussion

Ordinarily one does not associate any harmful effects with powder metallurgical operations, yet the possibility of occupational disease is far from remote as substantiated by the results of the investigations presented herewith. Whenever any manufacturing process using materials possessing toxic properties is placed on a production basis, a potential risk to employees' physical well being exists. In the present instance two very significant factors, the use of metallic lead in finely powdered form and recirculation of collected air, prompted the investigation which in turn pointed the way toward control of the hazard before any serious illness occurred. The experience described also illustrates the importance of the routine industrial hygiene survey in bringing to light such unsuspected dangers. In this particular instance management was operating under a false sense of security in the belief that the hazard was properly controlled by the individual dust collectors which had been installed at no small expense. Recirculation of air from collecting units provides a strong appeal to management because of the economy it offers. This study showed, however, that excessive amounts of toxic material may be recirculated with the returned air. It is apparent that the safest and most practical way of keeping air-

borne concentrations below levels which result in high lead absorption is to install suitable equipment for the collection and exhaust of contaminated air, to provide the necessary volume of heated make-up air to guarantee its efficient operation, and to institute good hygiene and safety practices.

Summary

A study was made in a small powder metallurgical plant in which collected air containing

metallic lead dust of extremely small particle size was recirculated. Although lead was present in small amounts (6% maximum) in the materials used, the survey revealed excessive amounts of lead in the returned air from unit collectors and in the atmosphere as well as high levels in the urines of exposed workers. Prompt control of the exposure by suitable exhaust ventilation and other precautionary measures eliminated the hazard before any cases of lead intoxication occurred.

SUPPLEMENT TO RADIATION HANDBOOKS

AN EIGHT-PAGE supplement to the NBS Handbooks dealing with radiation protection and related matters has been prepared by the National Committee on Radiation Protection and Measurements (NCRP). Entitled *Maximum Permissible Radiation Exposures for Man*, the supplement summarizes the new recommendations of the NCRP on safe limits of radiation exposure; it extends and clarifies the Preliminary Statement issued by the Committee in January 1957. The new publication introduces only minor changes and is intended to be in general conformity with the philosophy expressed in the April 1956 statements of the International Commission on Radiological Protection (ICRP).

The recommendations of the NCRP are regularly published in the NBS Handbooks, several of which are now being revised to bring them into conformity with the new recommendations. Pending the availability of revised Handbooks, the present supplement provides a simplified statement of the changes needed to comply with the new recommendations. Handbooks and the supplement are available from the Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C.

Free Silica Dust Concentrations Measured in Nine Brick Manufacturing Plants*

WILLIAM J. SCHREIBEIS† and LEE SCHREIBEIS, JR.††

Introduction

THE DUST exposures incident to the manufacture of fire clay and high silica bricks were determined in nine plants. The bases for initiating these studies were medical findings of chest x-ray examinations, but these data were not made available. Some indication of the magnitude of the silicosis problem in the silica brick industry may be had from the results of a study made by the Pennsylvania Department of Health in 1939.¹ This study revealed that 51.9% of the 1,035 workers examined had silicosis.

The operations in the manufacture of refractory brick are similar throughout the industry. The raw materials, which may come from mines or open quarries, include various clays, gravel and sand. The fire clay brick are formed from the clays and may have a total silica content of from 30 to 75 per cent. The high silica brick contain both clays and gravel or sand and have a total silica content of more than 95 per cent.

The mined or quarried materials are delivered by conveyor and chute to a crusher where larger pieces are reduced to a size of about one inch or less. Crushed clays, gravel, sand and pieces of fired brick, called grog, are fed to dry or wet pan grinders for further size reduction and moisture addition. The ground materials are elevated to vibrating screens from which oversized particles are returned to the grinders and fines are transported to the brick presses. In some plants the screened fines from different clays are stored in various bins for later mixing prior to pressing.

The green brick delivered from the presses are given a preliminary oven drying and then transferred to either a periodic or a tunnel kiln. The operation of placing brick in a periodic kiln is called "setting". The fired brick from the kiln are placed in storage or freight cars and trucks. This operation is referred to as "drawing". In cases where special forms of brick are

made further grinding of the fired brick is required to provide accurate dimensions.

Methods

The evaluation of the degree of exposure of men employed in the several operations was made on the basis of the results of samples collected for free silica determination and for airborne dust concentrations. Forty-one samples of dust were collected on filter paper for the free silica determination. (The filtering area was approximately 1.25 ft² and the sampling rate ranged from 30 to 45 cfm. An adequate sample was collected within one-half to three hours depending on the dust loading.) The dust on the filter paper was removed and suspended in ethanol, and particles less than about five microns in size—the respirable size—were siphoned off and collected. Microscopic examination of this dust was made to assure that the particles were less than five microns. This fraction of the total dust sample was analyzed by x-ray diffraction for the quantitative determination of crystalline free silica and other constituents present.

The dust concentrations were determined by a standard method using n-propyl alcohol as a collection medium in the midget impinger apparatus. A microscopic light field examination at 100 \times magnification was made using the MSA dust counting cell, a 20-minute settling period, and the necessary dilution of two portions of each impinger sample. Only particles less than five microns in size were counted.

Results

In discussing the results found in the nine plants surveyed, the data have been grouped as follows.

I. Two fire clay brick plants having high dust concentrations with low free silica content.

II. Six fire clay brick plants having lower dust concentrations and higher free silica content than the first two plants.

III. One plant manufacturing high silica brick with extremely high free-silica-bearing dusts in certain operations.

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Free Silica Content

The crystalline free silica concentrations determined from the respirable size of dust arising from the various operations in the nine plants are tabulated in Table I. Two of the fire clay brick plants, Group I, had somewhat lower free silica concentrations, and, as will be shown later, higher dust concentrations. In the grinding, screening, and mixing operations in these two plants the crystalline free silica content of the respirable air-borne dust ranged from 3 to 5 per cent in seven samples. Handling and grinding the fired brick resulted in air-borne respirable dust whose free silica content was 10 per cent in each of four samples collected. In each plant the free silica content of the air-borne respirable dust increased from about 5 per cent in the raw materials to 10 per cent in the fired product.

The results of free silica concentrations in Group II, which contains six fire clay brick plants, are tabulated in the center columns of Table I. The concentration of free silica in the respirable sized dust of 24 samples did not exceed 20 per cent. The free silica content of the dust arising from raw materials processing was not significantly different than the dust arising from handling the fired brick in each of the plants.

In the one plant manufacturing high silica brick, six samples were collected for the determination of the free silica content, and the results are given in the right hand columns of Table I. The composition of air-borne dust collected in the areas where raw materials were handled ranged from 5 to 15 per cent crystalline free silica as quartz. However, the free silica con-

tent of dusts in the areas where fired brick were handled were 85 and 90 per cent. These high percentages of free silica included significant amounts of the tridymite and cristobolite forms.

Dust Concentrations

In Table II the results of dust concentrations measured in the various operations of each group are given. In Group I (two plants) the dust concentrations averaged well above 50 mppcf for the crushing, grinding, screening and mixing operations. Since the free silica content of these dusts was only about 5 per cent, the recommended threshold concentration, adopted by the American Conference of Governmental Industrial Hygienists, of 50 mppcf was used as a basis for evaluating the degree of the exposure. Although low free silica dusts (5% or less) are classified as nuisance type dusts, the massive concentrations evidenced in these two plants might constitute a potential silicosis hazard.

In the pressing, drawing and grinding of brick in the two plants of Group I, the dust levels were below 20 mppcf. The free silica content of these dusts ranged from 5 to 10 per cent, and the recommended threshold limit for dusts of this character is 20 mppcf. Consequently, it was concluded that these operations were not giving rise to a silicosis hazard.

The dust concentration results obtained in the six plants of Group II are given in the center columns of Table II. The recommended threshold limit value for all operations in this group was 20 mppcf since the free silica content of these various dusts ranged from 7 to 20 per cent.

TABLE I
Crystalline Free Silica Concentrations of the Respirable Size of Dust From 41 Air-Borne Dust Samples Collected on Filter Paper at Various Operations

Operation	Group I		Group II		Group III	
	Fire Clay Brick—2 Plants		Fire Clay Brick—6 Plants		High Silica Brick—1 Plant	
	No. of samples	Free silica content %	No. of samples	Free silica content %	No. of samples	Free silica content %
Crushing.....	—	—	1	7	—	—
Dry pan grinding.....	4	3 to 5	6	7 to 18	14	2
Screening.....	2	5	3	14 to 20	17	—
Mixing.....	1	5	1	17	—	5
Pressing.....	—	—	3	7 to 18	13	1
Setting brick.....	(Tunnel kilns)		4	12 to 15	14	1
Drawing brick.....	1	10	6	8 to 15	11	1
Grinding brick.....	3	10	—	—	—	—

Note: * 44% tridymite, 13% cristobolite, and 28% quartz.

† 30% cristobolite and 60% tridymite. No quartz measured.

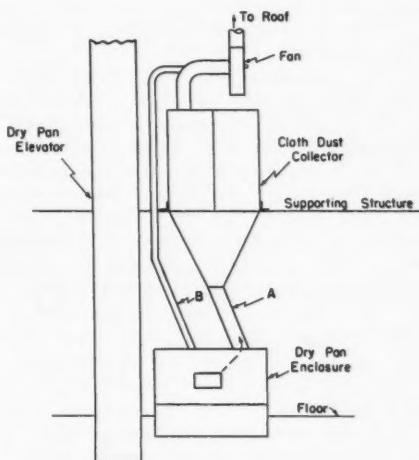
TABLE II
Total Dust Concentrations* Measured in Various Operations

Operation	Group I			Group II			Group III		
	Fire Clay Brick—2 Plants		No. of samples	Fire Clay Brick—6 Plants		No. of samples	High Silica Brick—1 Plant		
	No. of samples	Dust concentrations mppcf*		range	average		range	average	
Crushing.....	9	5.6 to 210	80	24	5.2 to 173	39	5	5.2 to 9.5	7.0
Dry pan grinding.....	13	7.6 to 705	122	31	6.3 to 225	46	7	6.1 to 95	30
Screening.....	10	10 to 418	99	25	6.4 to 53	21	—	—	—
Mixing.....	16	6.8 to 365	67	7	4.6 to 23	15	(7)	(6.1 to 95)	(30)
Pressing.....	8	1.5 to 14	7.3	23	2.2 to 16	7.2	6	0.9 to 7.8	5.5
Setting brick.....		(Tunnel Kilns)		19	2.2 to 46	12	4	2.7 to 9.5	4.8
Drawing brick.....	4	2.1 to 3.9	3.3	27	1.3 to 15	5.9	7	2.3 to 11.2	6.9
Grinding brick.....	7	3.2 to 18	9.9	—	—	—	—	—	—

* Dust concentration expressed in mppcf = millions of dust particles ($<5\mu$ in size) per cubic foot of air sampled.

Here again, the crushing, grinding and screening operations were found to liberate dust in concentrations higher than desirable in four of the six plants. The mixing, pressing, setting and drawing of brick from periodic kilns were operations in which the dust levels were well below the threshold limit value in 74 of the 76 samples collected. Thus, the silicosis hazard was considered to be low in these operations.

The dust concentrations in the high silica brick plant, Group III, are given in the right hand columns of Table II. The free silica content of the air-borne respirable dust in the crushing, grinding, mixing and pressing operations ranged from 5 to 15 per cent. Thus, a recommended threshold limit of 20 mppcf was used as the basis for considering whether a silicosis hazard existed. The dry pan grinding and mixing facilities in this plant produced dust concentrations in excess of the threshold



A=12" Combination Exhaust Duct and Chute for Discharge of collected Dust.

B=6" By-pass Duct for Exhaust During Shakeout.

FIGURE 2. Dust control system for dry pans.

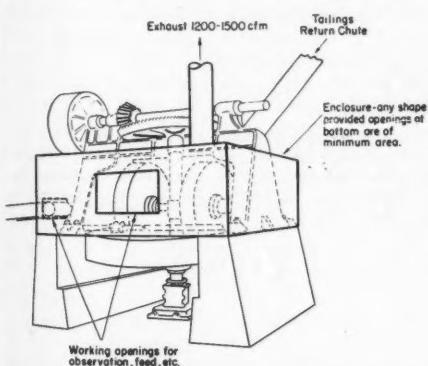


FIGURE 1. Enclosure for dry pan and exhaust.

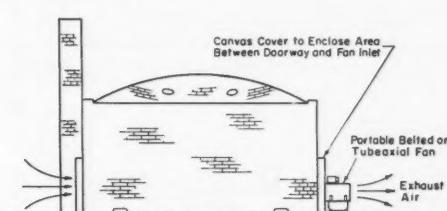


FIGURE 3. Ventilation of periodic kiln.

limit value, but the crushing and pressing operations were low dust producers.

The extremely high free silica content (85 and 90%) of the respirable air-borne dust in the setting and drawing of brick from the periodic kilns indicated the use of a threshold limit of 5 mppef. The dust concentrations found in the setting (average 4.8 mppef) and drawing of brick (average 6.9 mppef) were in the range which indicated a borderline health hazard.

Control Methods

The operations studied in this survey of nine plants which were associated with potentially hazardous dust exposures in one or more of the plants were: (1) crushing; (2) dry pan grinding; (3) screening; (4) mixing; (5) setting; and (6) drawing brick from periodic kilns. Control measures were recommended for each piece of equipment or operation where measured dust exposures were found to be higher than desirable.

In the crushing operations, three of the nine plants had high dust levels. The moisture content, and perhaps the season of year in which the mining is done, have a direct influence on the dust levels associated with this operation. The air-borne dust results from the dumping of the loaded mine cars and disturbances of settled dust in the area, as well as from the crusher action. Some crushing operations are located in the open, and in all such instances in this survey, the natural ventilation, together with other factors, produced acceptable dust levels. In the three plants with high dust levels, the crushers were located inside a building and isolated from the other operations. The dust control measures recommended for these operations included local exhaust hoods over the mine car dumping site and the crusher as well as equipment for collecting the dust.

Five of the nine dry pan grinding operations produced excessive dust exposures and were contaminating other work areas of the plants. This operation was considered to produce a most serious hazard and involved the greatest number of workmen. In Figure 1, a sketch of a typical dry pan is shown with an enclosure and exhaust connection recommended for the ventila-

tion of each dry pan. The enclosure has been constructed of wood, and is fitted around the structure of the dry pan so that a minimum open area exists. Figure 2 shows an over-all view of the collecting and exhausting system which employs bag dust collectors.

The screening operations in five of the nine plants resulted in high dust levels. Screens are frequently located above the dry pans, receiving dust laden air from this operation and generating considerable dust clouds in addition to that from the dry pans. More modern vibrating screens are equipped with enclosures and provisions for exhausting dust and air. In those plants equipped with this newer equipment, the dust levels were acceptable.

At the mixing operations in three plants, various clays were blended by agitation prior to pressing. In one of these three plants the dust levels were extremely high but were mainly the result of contamination from nearby dry pan and screening operations.

Periodic kilns were used in seven of the nine plants. In two plants the dust exposures during setting and drawing brick from the kilns were found to be higher than desirable. The method of control for this operation is shown in Figure 3. The principle is simply to dilute the comparatively stagnant and dust laden air within the kiln with less dusty outside air.

Dust concentrations in the pressing operations in each of the nine plants were found to be well below the recommended threshold limit value.

It is unfortunate that the opportunity to check the effectiveness of the dust control measures has not been obtained up to this time. We are unable to report on this important phase of an industrial hygiene study, but have considered the data herewith presented to be useful in showing the magnitudes of free silica composition and dust count levels found in nine plants of the refractory industry.

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Tunneling Operations in Massachusetts— Hygienic Aspects

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SINCE 1954 there have been two large tunneling operations carried on in Massachusetts. Both of these operations were located in the metropolitan Boston area, one being the extension of the main water supply system, and the other the construction of a main drainage sewer tunnel.

The City Water Tunnel Extension was constructed to increase and extend the present water supply of the City of Boston and its suburbs. The present water supply for metropolitan Boston is from Quabbin Reservoir located near Ware, Massachusetts, some seventy miles away. Water is fed to Boston via the Hultman aqueduct to Auburndale, and subsequently pumped to various parts of the city. Contract No. 193, City Tunnel Extension, specified construction of a concrete water tunnel from Shaft No. 7 in Brookline, through Brighton, to Shaft No. 8 in Allston, and to extend through Shaft No. 9 in Somerville, to Shaft No. 9A which is located in Malden.

Construction began on the City Water Tunnel Extension in April, 1954, and took approximately 3½ years to complete. The total distance was 37,219 feet or approximately seven miles. The tunnel was driven through country rock and is called a "deep" rock tunnel. This was done because a rock tunnel is not only more economical and faster to construct, but is superior in withstanding pressure.

The Boston Main Drainage Tunnel was constructed to handle sewage from the metropolitan area to a proposed sewage plant on Deer Island. Shaft A was constructed in Roxbury, Shaft B at Columbia Circle, South Boston, and Shaft C at Deer Island. The total length of the tunnel was some 37,586 feet or 7.12 miles. The depth of the tunnel was approximately 320 feet, and had a one-percent slope. This tunnel took somewhat over three years to complete.

The two tunnels were essentially the same in their construction. The rough diameters of the tunnels ranged from 14 to 15½ feet, and the completed concrete tubes were 10 and 11

feet in diameter, respectively, with concrete averaging one foot in thickness.

Shaft Sinking

First in the series of operations was that of shaft sinking. The rough diameter of the shafts ranged from 11 feet to 16 feet. Top-soil was removed and all loose dirt excavated. Wet pneumatic hand drills were used to drill vertical holes in the bottom. The amount of dust produced in this operation was normally less than in tunneling because drilling was vertical and the bottom of the shaft was wet. The holes were loaded with dynamite which was subsequently exploded to break the rock. The resulting muck was removed and the cycle was repeated. Air was fed into the shaft under positive pressure after the blast to clear the atmosphere of blasting fumes, and also during drilling, to remove dust from the drilling operation. A minimum ventilation rate of five hundred cubic feet of air per minute per drill was used.

Drilling

Drilling was done with "jumbo"-mounted pneumatic drills. Five drills were mounted on the "jumbo" which was brought to the heading on a small railroad track. Bits were of carballyoy steel 1¾ inches in diameter and the holes were usually drilled eight feet deep. At least thirty-five holes were drilled in the heading, which took about forty-five minutes drilling time. Three drilling cycles were usually accomplished each shift, so that the total drilling time per shift was 2½ hours. All drilling was done wet and no dry drilling was allowed under any conditions.

Blasting

At the completion of the drilling operation, the holes were loaded with dynamite. Electric delayed blasting caps were used and the charge was detonated from some one thousand feet, or more, away. The charge was usually fired in

ten delays and the average shot consisted of about 140 to 275 pounds of dynamite, depending on the conditions encountered. The maximum amount of dynamite in any one delay rarely exceeded sixty pounds.

It was thought that appreciable quantities of unexploded nitroglycerine could possibly exist in the working atmosphere after the blast, because there were numerous complaints of headaches at the beginning of the operation. However, chemical air tests for nitroglycerine were taken at this time and the results were essentially negative directly after the blasting operation. Air tests for carbon monoxide and oxides of nitrogen were taken periodically so that a time schedule could be set up for the men to re-enter the area safely.

Mucking

Muck is the name given to the broken stone after a detonation has taken place. It consists largely of broken pieces of stone approximately an inch in diameter. However, stones a foot or more in diameter constitute an appreciable portion of the muck pile. This material was removed by means of a mucker which was brought to the heading on railroad tracks. The mucker consisted of a large electrically-operated scoop arrangement which picked up the muck and dropped it on a conveyor belt. The belt dropped



FIGURE 1. Mucking machine.



FIGURE 2. View of tunnel showing ventilation duct.

the muck into cars which were taken out to the shaft by electric locomotives. Figure 1 illustrates the mucking machine.

When the men re-entered the heading after a shot, their first duty was to wet down the muck pile and wash the face with a water hose. This served two purposes: (1) To reduce any atmospheric concentrations of oxides of nitrogen which might be present. (2) To suppress any dust which might arise from the subsequent mucking operation. These particular tunneling operations were rather wet from seepage, so that dust control during drilling and mucking was quite easily accomplished.

Ventilation

Ventilation was provided through spiral Naylor steel ducts, 26 inches in diameter, which extended to within 70 feet of the heading. Each heading was provided with a separate exhaust system which was located above ground. Two Axilflow Joy Fans, 3500 rpm, driven by 18-hp motors were provided for each system. The capacity of each fan ranged from 5000 cfm to 14,000 cfm. A minimum airflow of 6000 cfm was maintained by each system throughout the entire operation. At the outset, the fans were exhausting approximately 10,000 cfm from each heading. As the length of the tunnel progressed,

double boosters were installed in the fan line every 3000 feet. The efficiency of the ventilating system decreased but never fell below 6000 cfm. This gave a minimum ventilation rate of 1200 cfm per drill and cleared the heading of blasting gases within 25 minutes. Figure 2 shows the ventilation duct.

Prior to blasting, the ventilation duct was provided with a header to prevent damage to the pipe and subsequent leakage when additional lengths of pipe were added. The pipe was usually kept within 60 to 80 feet from the heading. The six-inch compressed air line with a two-inch nozzle was opened prior to the blast to agitate the blasting fumes and clear the heading more rapidly. The ventilating fan was drawing air from the tunnel at all times. A reversible system was not used because the men complained of drafts when air was supplied through the duct to the heading.

Various portable air-moving devices were tried at the heading to agitate the blasting fumes, to facilitate their removal more rapidly. These devices proved to be of very little value and were extremely cumbersome to set up. The use of compressed air for this purpose proved to be more desirable and certainly more convenient. The longest waiting time necessary before the men could re-enter the blast area was about 25 minutes under these conditions of operation. The waiting time necessary when the tunnel had only progressed a few hundred feet was approximately 15 minutes. Results of the air tests taken for blasting gases are given in Tables I and II.

TABLE I
Oxides of Nitrogen—Average Results Found

Test number	Time after blast (minutes)		Nitrogen dioxide ppm		
			High	Low	Average
1	1-5	End of ventilation duct (60-80 feet from heading)	40	3	19
2	5-10	Beyond ventilation duct (40-60 feet from heading)	21	4	16
3	10-15	On muck pile (20 feet from heading)	21	2	11
4	15-20	On muck pile (10-20 feet from heading)	10	1	4
5	20-25	On muck pile (10-20 feet from heading)	2	0	1
6	25-30	On muck pile (10-20 feet from heading)	0	0	0
Maximum Allowable Concentration			10		

TABLE II
Carbon Monoxide—Average Results Found

Test number	Time after blast (minutes)		Carbon monoxide ppm		
			High	Low	Average
1	1-5	End of ventilation duct (60-80 feet from heading)	250	100	200
2	5-10	Beyond ventilation duct (40-60 feet from heading)	200	100	175
3	10-15	On muck pile (20 feet from heading)	200	75	125
4	15-20	On muck pile (20 feet from heading)	100	0	50
5	20-25	On muck pile (10 feet from heading)	50	0	25
6	25-30	On muck pile (10 feet from heading)	0	0	Negligible
Maximum Allowable Concentration			100		

Atmospheric Testing Program

A program of air testing was undertaken by the Massachusetts Division of Occupational Hygiene to determine to what degree the workers were being subjected to atmospheric contaminants. During the tunnel-driving operations, the atmosphere was tested at regular intervals for dust, carbon monoxide, and oxides of nitrogen. During the drilling operation, dust counts were taken of the air at the operators' locations on the Jumbo and of the general air at the heading. These tests were taken with the M. S. A. Midgit Impinger and the standard light field method was employed in counting the samples. Results of these tests are given in Table III. A rock analysis, for free silica content, was made periodically by x-ray diffraction technique.

The rock was predominately an argillite or pre-argillite, and occasional quartz veins were encountered. The free silica content of the rock ranged from 10 per cent to 30 per cent. A maxi-

TABLE III
Rock Dust—Average Results Found

Test number		Rock dust mppcf		
		High	Low	Average
1	Operator's exposure drilling	10	.5	6
2	General air on "jumbo"	4	.5	3
3	Operator's exposure—Mucking	5	3	4
	Maximum Allowable Concentration			15

mum allowable concentration of fifteen million particles per cubic foot of air (mppcf) was set for this type rock.

At the completion of the drilling operation, the "jumbo" was taken back a safe distance from the heading before blasting. Air tests were made regularly after the blasting operation. Tests for carbon monoxide were made with an M. S. A. Carbon Monoxide Detector.

Tests for nitrogen dioxide were made by collecting atmospheric samples on silica gel and subsequently analyzing them for nitrate by the phenol disulfonic acid method.

It should be pointed out that these are average test results derived from many individual tests. The atmospheric dust concentrations during the drilling operation remained rather constant regardless of the length of the ventilation line.

Diesel Engines Underground

In tunneling operations the locomotives used for haulage are usually electric, and derive their power from storage batteries or a trolley line mounted overhead in the tunnel. The contractors had used battery-operated locomotives for hauling the muck out of the tunnels. However, when concreting operations began, the electric locomotives were found to be inadequate to haul the concrete up the one-per cent grade to the concreting operation. Permission from the Commissioner of Labor and Industries to use Diesel haulage equipment underground was asked by the contractors. Permission was granted provided the recommendations of the Massachusetts Division of Occupational Hygiene were met. The recommendations were as follows:

1. The Diesel locomotives shall be of the type approved by the Commissioner for use underground in non-coal mines.

2. Proper ventilation shall be provided to maintain a healthful work environment. (The fresh air reaching the area where the Diesel is operating is to flow constantly in one direction and shall amount to at least 75 cfm per Diesel

horsepower. The rate of dilution of the exhaust gases shall be 25 to 1.

3. Where explosive gases or dusts may be encountered, the intake and the exhaust openings of the engine must be protected by flame arrestors, and all flame passages or possible arc-producing parts must be enclosed in explosion-proof housings.

4. All surfaces must be maintained at temperatures below 400°F and other adequate precautions must be observed to eliminate fire hazards.

5. Adequate regular maintenance must be provided for haulage equipment in service.

6. The Diesel fuel for underground use shall have a flash point of not less than 150°F and contain not over 0.5% sulphur by weight.

7. The Diesel fuel supply shall not be stored or taken in the tunnel in amounts greater than required for one day's operation.

8. The exhaust for the Diesel engine shall be passed through a scrubber to reduce the health hazard and discomfort to the workers. Scrubbers shall be serviced at least once every eight hours of operation.

9. The undiluted exhaust gases from the Diesel shall not contain over 2500 ppm of carbon monoxide.

10. The working atmosphere should not contain over 20 ppm carbon monoxide, 2 ppm nitrogen dioxide, or sufficient aldehydes to cause undue irritation.

11. On operations where the ventilation system has been removed, a bulkhead shall be constructed and adequate mechanical exhaust maintained through the bulkhead to maintain a safe working atmosphere. The design and capacity of the fans and bulkhead shall be subject to the approval of the Commissioner.

An atmospheric testing program was instituted by the Division of Occupational Hygiene to determine the concentrations of Diesel exhaust gases that existed in the tunnel atmosphere. Tests were made routinely for carbon monoxide and oxides of nitrogen where the

TABLE IV
Diesel Exhaust Gases—Average Results Found

Test number		Carbon monoxide ppm			Nitrogen dioxide ppm		
		High	Low	Average	High	Low	Average
1	Six inches from exhaust pipe	50	0	25	30	2	18
2	Operator's exposure on Diesel	0	0	Negligible	0	0	Negligible
3	General air—three feet from exhaust pipe	0	0	Negligible	0	0	Negligible
	Maximum Allowable Concentration			100			2

Diesel equipment was being operated. Results of these tests are given in Table IV.

Diesel haulage equipment was used in both the tunnel driving operation and the concreting operation in the construction of the sewer tunnel. Diesel equipment was only used during the concreting operation in the water supply tunnel. In both cases no mechanical exhaust was provided in the tunnels during the concreting operations.

Although the tests indicated that the operators were exposed to insignificant quantities of carbon monoxide and oxides of nitrogen, eye and respiratory irritation could be experienced at times. This was believed due to the aldehydes in the Diesel exhaust. This was alleviated somewhat by keeping the water scrubbers full at all times and changing the water at more frequent intervals.

Conclusions

In these rock tunneling operations, there was a potential dust hazard from drilling, and fume hazard from blasting with dynamite.

The dust hazard from drilling was adequately controlled by the use of wet drills and a minimum ventilation rate of 1200 cfm per drill (6000 cfm for five drills). This was also adequate ventilation to clear the heading of blasting gases within 25 minutes after each blast.

The operation of Diesel haulage equipment did not present a real health hazard as long as the recommendations of the Division of Occupational Hygiene were followed. Aldehydes from the Diesel engines did present a nuisance prob-

lem at times, but was reduced by keeping the scrubbers at maximum efficiency.

At the outset of the tunneling operations, there were numerous complaints from the workers of headaches. The cause of the headaches was not definitely determined. However, when a waiting-time schedule after the blasting operation was established, the complaints subsided. It is possible that the headaches resulted from the inhalation of blasting fumes.

Acknowledgment

Special acknowledgment is made to Mr. George Day, Safety Engineer, Morrison-Knudsen Construction Company, whose exceptional cooperation aided greatly in making this study possible.

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COURSE FOR NURSES

A COURSE of training in industrial health for registered nurses is to be offered for the fifth consecutive year by the Institute of Industrial Health of the University of Cincinnati during the week of March 2, 1959. The objective of the course is to assist in the development of the administrative abilities of the industrial nurse and to provide the nurse with current concepts and practices in the field of occupational health. Didactic presentations will include an analysis of the nurse's own job; consideration of her in-plant and community relationship; and a description of her functions as they have to do with preventive and therapeutic programs. Current concepts regarding record keeping will also be discussed. Opportunity will be provided for informal discussion in work shop sessions.

Registration fee is \$45.00. A certificate of attendance will be awarded at completion of the course. For additional information write to Secretary, Institute of Industrial Health, Kettering Laboratory, Eden and Bethesda Avenue, Cincinnati 19, Ohio.

A Dynamic Apparatus for Preparing Air-Vapor Mixtures of Known Concentrations

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Introduction

KNOWN concentrations of air-vapor mixtures are indispensable to both toxicologists and industrial hygienists. Instrument calibration, absorption efficiencies, and development of analytical methods all depend on a ready supply of such mixtures. Toxicology experiments involving animal exposure to air-borne substances and physiological tests on humans also make use of the various techniques for dispersing vapors in air. These mixtures can be prepared by either static or dynamic systems. Both techniques have been previously described.¹⁻²⁵

Static Systems

Static techniques for preparing air-vapor mixtures are characterized by the batchwise addition of the liquid to be vaporized into a non-flowing, completely enclosed volume of air. The simplest such system is a large bottle tightly closed with a stopper through which pass glass entrance and exit tubes.¹ A calculated volume of the liquid to be vaporized is pipetted through the entrance tube; when evaporation is complete, an air sample is withdrawn and is replaced by outside air which dilutes the mixture. Variations in this simple technique have included the use of large chambers and even rooms² to contain the air-vapor mixtures. Electric fans are often used to assure thorough mixing. A further refinement utilizes a series of bottles, each filled with the same concentration of vapor and air so that the sample withdrawn from the first bottle is replaced, not by outside air, but by vapor-laden air from the second bottle in series.³ Yet another way to prevent the dilution of the air-vapor mixture with replacement air is to prepare the mixture in plastic bags. As the sample is withdrawn, the walls collapse and the interior thus remains at atmospheric pressure. Thus no replacement air is needed. Nor are static techniques confined to air-vapor mixtures, since gases may also be in-

jected into the sampling chamber by means of a glass syringe.⁴

Although simple and inexpensive, static systems have several disadvantages:

1. They are tedious to use. To attain maximum accuracy, the liquid to be vaporized must be added to the system by means of ampoules. These fragile bubbles of glass must be weighed, filled with liquid, sealed, reweighed and then placed either directly in the sampling chamber or in an ampoule crusher connected to the chamber. This is a time-consuming chore.
2. There is always a danger of implosion, since for proper vaporization of the liquid the bottles must be partially evacuated.
3. A static system is extremely inflexible. To change the concentration, the bottles must be purged with compressed air and the filling process repeated. Sufficient purging to assure minimal gas or vapor residue is important.
4. Many common solvents and gases adsorb heavily on the extensive interior surfaces of static chambers. This is particularly noticeable when low concentrations of vapors are being prepared.
5. Static systems are bulky. A set-up employing five 13-gallon bottles uses about 20 square feet of bench space.

To summarize, static systems may be simple and inexpensive, but in use they prove cumbersome, tedious, and time consuming, and are so inflexible that their frequent use is discouraged. Moreover, adsorption makes suspect many results obtained with such a system.

Dynamic Systems

All dynamic systems operate by continuously injecting a gas or vapor into a moving stream of air in order to have a constant supply of the mixture. The simplest such system is often used in toxicology experiments. Air is bubbled through a gas-washing bottle or atomizer containing the

liquid to be vaporized; the resulting air-vapor mixture is then passed into the sampling chamber with the vapor concentration being controlled by the rate of air flow and the weight of liquid vaporized. Variations in these "gravimetric" techniques have been reported by Olsen⁴ and Gisclard.⁵ Care must be taken to insert several traps between the vaporizing vessel and the sampling chamber and the weight of settled material caught in these traps should be subtracted from the weight of vaporized liquid.

To better control the rate of volatilization, Silverman proposed the use of a simple syringe injection device by means of which concentrations of vapors can be easily produced.⁶ Amdur reported a refinement of this in a device used for generating sulfuric acid mists.⁷ Modifications of dynamic methods for preparing air-gas mixtures have been described by Lewis and Koepf,⁸ and by Silverman.⁹

The advantages of a dynamic system are numerous:

1. First, there is an abundant and continuous supply of the mixture.
2. Swift changes in concentration are effected by altering either the temperature or rate of feed of the liquid being vaporized or by changing the air flow rate. Such changes require only a few minutes compared with the half hour or more needed to effect a similar change in a five-bottle static system.
3. Purging is normally very simple since a dynamic system reaches equilibrium rapidly. The time in minutes (t_{99}) required to purge to 99% freedom from vapor can be calculated from the equation:

$$t_{99} = \frac{4.605 \times \text{chamber volume in liters}^{10}}{\text{liters/minute thru chamber}}$$

This is also the time required to reach equilibrium after a concentration change.

4. Concentrations are easily controlled within the limits normally required by the industrial hygienist.
5. In animal exposure experiments, a dynamic system assures ample oxygen supply and sweeps waste respiratory products from the chamber.
6. The adsorption problem is negligible since vapor adsorbed on the walls reaches equilibrium with vapor in the air stream.
7. Such an apparatus can be very compact, requiring little space in the laboratory.
8. Finally, because of its flexibility and convenience, laboratory personnel are encour-

aged to use a dynamic system as an everyday tool.

A Dynamic Air Blender

Figure 1 shows an overall view of the air blender, a dynamic apparatus which has been used extensively for preparing air-vapor mixtures. It is assembled from readily available components and can be made for approximately \$250.00.

Liquid to be vaporized is injected into the system with the Gilmont¹¹ ultra-micro burette (Emil Greiner Company, Catalog No. G-15390) which can be seen in the upper right. To the tip of this burette has been sealed a glass connecting arm, having glass ball and socket joints at each end. To the lower joint is clamped a standard jacketed condenser which serves as the vaporizing chamber for the liquid. The condenser may be warmed by either steam or hot water. The top joint of the connecting arm is clamped to an arm of a Kjeldahl trap, which in turn has been sealed to a long glass tube which serves as the sampling chamber. Air from a compressed air line is metered through the rotameter shown below the burette and then goes through the condenser and past the burette tip where the

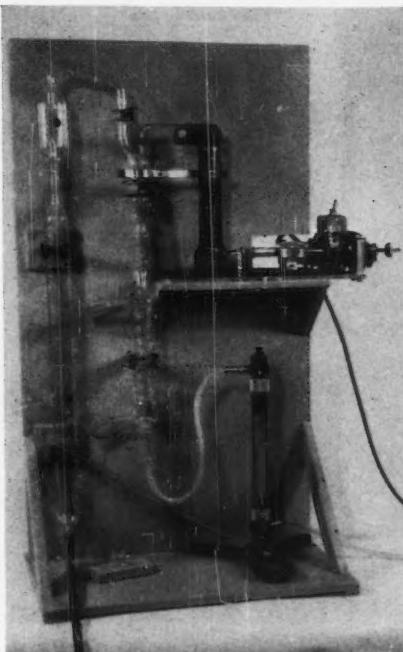


FIGURE 1. Over-all view of the air blender.

liquid is vaporized in the air stream. With an air flow of 0.1 cfm, concentration changes can be made in one minute and the chamber can be purged in the same length of time.

Figure 2 shows a close-up of the burette tip and Kjeldahl trap. The Kjeldahl trap is used to cause turbulence in the air stream and thus helps to mix the vapor with the air. A close-up of the Gilmont burette is given in Figure 3.

To fill the burette, a small shelf is plugged into the framework supporting the burette and a beaker containing the solvent to be vaporized is placed on the shelf so that the burette tip is completely immersed. The burette plunger is then manually turned until a drop of the displaced mercury is visible at the burette tip. The plunger is then reversed, drawing the solvent into the burette. The beaker of solvent and shelf are then removed, the burette tip is wiped dry

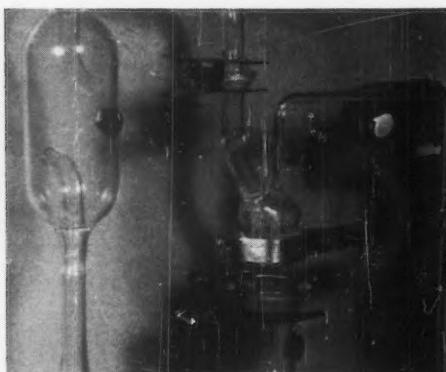


FIGURE 2. Close-up view of the mixing and vaporizing chambers. Note burette tip below lower clamp.



FIGURE 3. Close-up view of the modified Gilmont ultramicroburette.

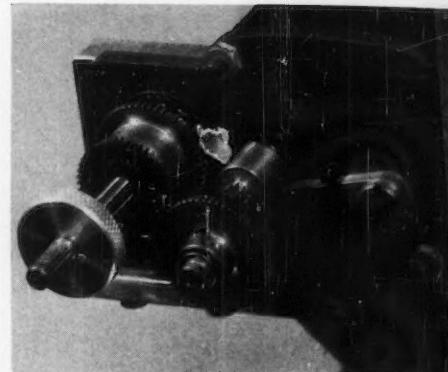


FIGURE 4. Gear train adjusted for slow delivery rate.

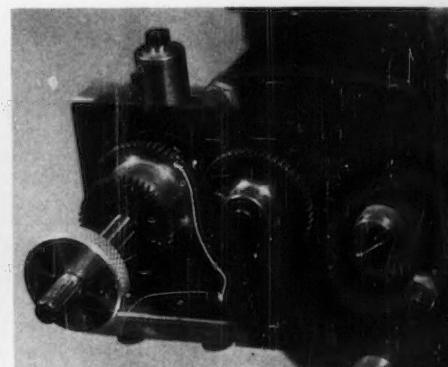


FIGURE 5. Gear train adjusted for fast delivery rate.

and the condenser is clamped to the connecting arm. The air blender is now ready to use.

The original manual operation of the burette has been modified by the addition of a reversible 1 rpm Bodine Motor. This motor is connected to the burette plunger by means of three driving gears which can be changed to permit two forward speeds. The gear system as shown in Figure 4 is set up at slow speed; this permits the delivery from the burette tip of 0.0007 milliliter of solvent per minute. To use the motor drive for the faster of the two delivery rates, 0.0031 milliliters per minute, the gears are arranged as shown in Figure 5. A working drawing of this gear system, plus photographs and a description of the work involved will be sent on request.

A micro-switch was installed which engages an arm on the burette shaft. This stops the

motor shortly before the end of travel and prevents jamming the mechanism. This arm can be seen projecting down from the shaft in Figure 3. The micro-switch arm is also visible.

Applications of the Air Blender

Establishing odor thresholds. One of the more unusual applications of this apparatus has been to prepare air-vapor mixtures in an effort to determine the minimum identifiable odor of various common solvents. We claim no more than a rough approximation but feel that data so obtained is in the right order of magnitude. We are forced to agree, however, with McCord and Witheridge that "repeated testing on different days is likely to disclose a varying capacity for odor detection in the same individual".¹² This daily variation in our own ability to detect odors was quite evident. In Table I appear minimum identifiable odor levels obtained with the air blender. Figure 6 shows the blender used for this purpose. The levels shown represent the average response of three different individuals. It is interesting to note the rather high concentration of methyl alcohol which must be present before its odor is noticeable. This is over seven times the presently accepted MAC of 200 ppm. It has been noted during actual field sampling that a level of 2,000 ppm of methyl alcohol was barely detectable by odor.

Mass spectrometer calibration. The air blender was first used in the Kodak Research Laboratories for preparing mass spectrometer calibration samples. A 50 cc, twin-stoppered sampling bulb to one end of which has been fused a 7/25 standard tapered joint fits into the sampling port at the lower left end of the sampling chamber. A similar joint on the mass spectrometer permits the bulb of vapor sample to be connected directly.

TABLE I

Minimum Identifiable Odor Levels Determined with the Air Blender

Solvent	M. I. O. (ppm)
Methyl alcohol	1500
Chloroform	1400
Acetone	800
Methylene chloride	450
Ethyl alcohol	350
Methyl chloroform	300
Isopropyl alcohol	200
Ethylene chloride	200
Trichloroethylene	75
Ether	70
Butyl acetate	20
Butyl alcohol	15



FIGURE 6. Determining minimum identifiable odors with the air blender.

Method development. A connecting tube having a 7/25 standard taper male fitting at one end and a ball joint at the other is used to connect the air blender to an all-glass sampling unit consisting of two gas-washing bottles arranged in series. A set-up such as this was used to develop an analytical method for acetic acid vapor in air¹³ and is also used for determining collection efficiencies in various absorbing media. A laboratory jack has been found useful in lining up the bubbler bottles with the sampling port. In an arrangement such as this it is wise to keep the sampling rate at no greater than two-thirds of the air flow through the air blender apparatus.

TABLE II

Concentration Ranges of Common Air-Vapor Mixtures Which Can Be Prepared with Air Blender

Solvent	MAC (ppm)	Concentration Range* (ppm)	
		Low	High
Benzene	25	6	850
Methyl alcohol	200	12	1870
Acetic acid (undiluted)	10	9*	1320
Acetone	1000	7	1025
Methyl chloroform	500	5	760
Carbon tetrachloride	25	5	780

*Air blender parameters upon which above figures are based were as follows:

Air flow through blender (cc/min)	35,400	1,060
Blender delivery rate (ml/min)	0.0007	0.0031

When a solvent has a low MAC, it is often necessary to dilute it with an inert solvent. For example, one part acetic acid plus nine parts of acetone would permit the low range to be extended down to 0.9 ppm.

Extremely low concentrations may be attained in the air blender by using the slow speed delivery rate as well as a high air flow through the blender. Even lower concentrations may be attained by using these techniques plus a further trick: this consists of diluting the material to be vaporized with a solvent which is inert to both this material and to the reagents employed for the analytical determination.

Table II shows the concentration ranges of some common air-vapor mixtures which have been prepared with the air blender.

Instrument calibration. Serious errors can result from failure to calibrate frequently air sampling equipment. We have found the air blender to be extremely useful for this work. We calibrate many of our instruments immediately before or after every job in the field. We have found that some of the commercially available squeeze bulb air samplers may be subject to variations in the chemical components. Calibrating such an instrument permits the variations to be known and thus a suitable correction factor may be incorporated into the readings.

Summary

There are many ways to prepare mixtures of contaminants in air and all methods are either simple or complex variations of the two fundamental techniques—static and dynamic. A dynamic apparatus such as the air blender herein described offers a simple and convenient way to synthesize air-vapor mixtures of known concentrations. It may be assembled from readily available components at minimum cost and should prove particularly useful to industrial hygienists.

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Studies on Aromatic Amines. I. Preliminary Observations on Benzidine Metabolism

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Introduction

SOME features of aromatic amine metabolism involving hydroxylation of the aromatic ring followed by conjugation with sulfate or glucuronic acid have been described.¹ Data leading to these conclusions have been collected almost entirely by isolation techniques. A difficulty with such information is that it is rarely quantitative and does not provide certainty about additional unidentified metabolites. The need for quantitation and complete cataloging of all metabolites is increased by our inability at present to explain the occurrence of bladder cancer in man and dog as the result of exposure to certain aromatic amines in contrast to the resistance of all other species tested with the same compounds. Since bladder cancer is presumably caused by a urinary metabolite, a metabolite peculiar to man and dog would be expected but has not been observed.

A method of assaying amine metabolites has been developed which depends on the formation of a colored naphthoquinone derivative. The advantages of this procedure over others examined were that stable derivatives capable of separation by a number of techniques were quantitatively formed with a variety of aromatic amines and their metabolites. The reaction appears to be generally applicable to aromatic compounds with unsubstituted amino groups. The method has been applied to the identification of urinary metabolites of benzidine in the dog and rabbit, and to a preliminary survey of the metabolites of a group of carcinogenic and non-carcinogenic aromatic amines in the dog and rabbit.

Experimental and Results

NAPHTHOQUINONE DERIVATIVE METHOD

Since the approach of forming a suitable derivative had been successfully used with the amino acids the reagents so used were tried initially. One of these, 2,4-dinitrofluorobenzene formed oils with benzidine and the reagent could not be readily separated from the derivative. The reaction with beta naphthoquinone-4-sul-

fonate (NQS) appeared more useful. The reaction of this compound (Figure 1) with aromatic amines was initially reported by Boeniger.² Aromatic amines react rapidly in the range pH 2 to 9, while the reaction with amino acids and other aliphatic amines does not occur below pH 5.³

The aromatic amine derivative is insoluble in water but goes readily into solution above pH 10. The derivative is completely extracted from acidic solution into benzyl alcohol leaving the excess NQS behind in the water layer. The compounds listed in Table I were prepared by reacting the aromatic amine with a five-fold excess of NQS at pH 2. The product was collected by centrifugation, washed with 0.01 M hydrochloric acid until the washing was colorless, then dried in a vacuum desiccator. The nitrogen equivalent weight (from nitrogen content determined by micro Kjeldahl) in comparison with the theoretical, and the millimolar extinction coefficient at 470 m μ are listed in Table I. It is apparent that the optical extinction bears a uniform relationship to the number of amino groups, and that analogous chemical products are formed with the various aromatic amines tested.

This reaction of aromatic amines with NQS was utilized to measure aromatic amine metabolites quantitatively and to aid in the identification of the metabolites of benzidine.

The quantitative application of this procedure is carried out as follows: NQS is recrystallized from the commercial product according to Folin.⁴ A 0.02 M solution of NQS in 0.01 N hydrochloric acid is prepared weekly and kept under refrigeration. The urine is adjusted to pH 3. To three milliliters of urine containing from 0.1 to 5 micromoles of aromatic amine is added one milliliter of the 0.02 M NQS reagent in 0.01 M hydrochloric acid in a screw cap test tube. After five minutes the solution is extracted by shaking with three milliliters of benzyl alcohol, the mixture centrifuged and the water layer discarded. The alcohol layer is re-extracted three times with 0.01 N hydrochloric acid, centrifuged and the water layers again discarded. An aliquot of the benzyl alcohol is diluted with

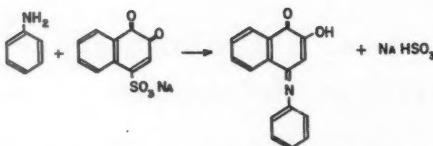


FIGURE 1. Reaction of aniline with 1,2 naphthoquinone-4-sulfonate.

TABLE I
Comparison of Naphthoquinone
Amine Derivatives

Naphthoquinone derivative	Theoretical nitrogen equivalent	Observed nitrogen equivalent	Millimolar extinction per nitrogen equivalent 470 m μ
Aniline	249	253	5.45
Benzidine	248	250	5.20
3-Hydroxy benzidine	265	270	5.50
3-Sulfate benzidine	344	345	5.15
2-Naphthylamine	299	301	5.42

95% ethanol to a suitable color intensity (1:1:5). Normal urines from the human, dog, rabbit, and guinea pig gave zero values by this procedure. Recovery of aromatic amine when added to urine was from 99–101% with aniline, benzidine, and benzidine-3-sulfate ester.*

BENZIDINE METABOLITES

Benzidine-hydrochloride was dissolved in water and injected intraperitoneally in dogs and rabbits. The usual dose employed was 1 gm for a 20 kg dog, 100–300 mg for 5 kg rabbits. The animals were kept in metabolism cages and the urine was collected under toluene.

Urinary metabolites of benzidine were divided into ether extractable compounds and those which remained in the water phase.

Ether Extractable Benzidine Metabolites: The ether portion was evaporated under a stream of nitrogen. The amine was dissolved in 0.01 N HCl and treated with NQS as described above. The benzyl alcohol layer was then extracted two times with 0.1 N sodium hydroxide. Under these circumstances the authentic NQS derivatives of synthetic 3-hydroxy benzidine* and 3,3'-dihydroxybenzidine** distributed into the alkali, while NQS benzidine remained in the alcohol

* 3-Hydroxybenzidine and the sulfate ester of this compound were synthesized by Dr. Herb Weinfeld. The 3-hydroxybenzidine was prepared by treating 3-ethoxy-benzidine with 40% HI. The sulfate ester was prepared from this compound by reaction with chlorosulfonic acid in pyridine.

** 3,3' dihydroxybenzidine was a gift from the National Aniline Division.

phase. The unesterified hydroxylated derivatives turned purple in alkali and could be measured colorimetrically by reacidification and extraction into benzyl alcohol. Recovery experiments carried out with this procedure gave 90% recovery for the hydroxylated derivatives and 100% for benzidine.

When this procedure was applied to dog and rabbit urines small quantities of unmetabolized benzidine were usually observed, but no purple derivatives were found in the alkali as would be the case if measurable amounts of unesterified hydroxy metabolites were present.

With dog urines a portion of the NQS derivative of the ether soluble fraction was extracted into the alkali, but did not turn purple. That this material was not an unesterified hydroxy metabolite was further confirmed by paper chromatography with 80% propanol, where the unknown NQS derivative had an *R*_F of 0.3 while reference hydroxylated compounds did not leave the origin. The nature of this material is being studied and will be reported later.

Water Soluble Benzidine Metabolites: Separation of NQS derivatives was initially attempted by precipitation at selected pH's. This procedure provided a useful method of isolating NQS derivatives; however, solvent partition was used for quantitative separation.

The presence of both glucuronide and sulfate esters of 3-hydroxy benzidine was established in the dog and rabbit urine after administration of benzidine as follows:

The NQS derivatives were precipitated from urine by adjusting the urine to pH 2 and adding 5 mg of NQS per milliliter of urine. The precipitate was collected and washed three times with an equal volume of 0.01 N hydrochloric acid. The precipitate was then dissolved in 0.1 N sodium hydroxide and adjusted to selected pH's and the precipitates collected.

It was observed that 90% of the rabbit NQS derivatives were precipitated at pH 4, while only 17% of the dog metabolites precipitated at this pH. The remainder was precipitated at pH 2. The precipitate obtained from rabbit urine at pH 4 was dissolved at pH 6 and precipitated at pH 5. This procedure was repeated three times. This material was identified as the NQS derivative of the glucuronide of 3-hydroxybenzidine by the following observations:

(1) Glucuronidase (Worthington) at pH 6 yielded the NQS derivative of 3-hydroxybenzidine plus a material which gave a positive Tollens test.

(2) The titration curve of the compound showed two points of inflection, one at pH 8 where the neutralization equivalent was

400, and a second at pH 4 where the neutralization equivalent was 790.

These are in good agreement with the predicted values for the glucuronide which would have two phenolic groups and one carboxyl group. For quantitative determination, advantage was taken of the observation that this compound is completely extracted by a benzyl or amyl alcohol from 0.1 N sodium hydroxide while the sulfate ester remains in the water phase.

The NQS derivative of the 3-sulfate ester of benzidine was isolated from both dog and rabbit urine by dissolving the NQS derivatives in 0.1 N sodium hydroxide, extracting with benzyl alcohol, bringing the solution to pH 9 with the addition of boric acid, extracting with amyl alcohol and precipitating with ether. The infrared spectrum of this material was found to be identical with the authentic NQS derivative prepared from the synthetic 3-sulfate ester of benzidine (Figure 2).

The quantitative urinary excretion of metabolites after administration of benzidine to the dog, rabbit, and guinea pig are summarized in Figure 3.

It can be seen that total recovery of metabolites in the rodent urine was substantially less than from dog urine. This may be due to con-

jugation of the amino group by the rodents with acetyl, glucuronide or sulfamate,⁵ thereby making it non-reactive to NQS. We observed that rabbit urine reduced Benedict reagent while dog

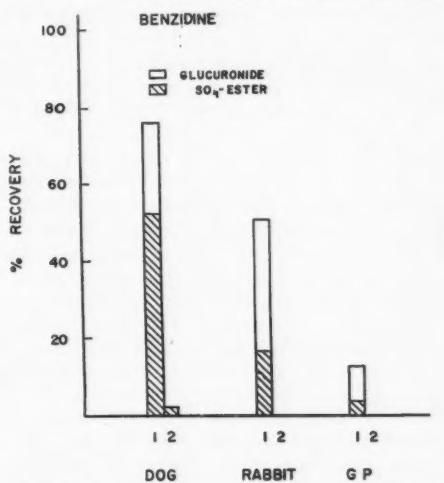


FIGURE 3. Recovery of benzidine-3-sulfate and benzidine-3-hydroxy glucuronide in dog, rabbit and guinea pig.

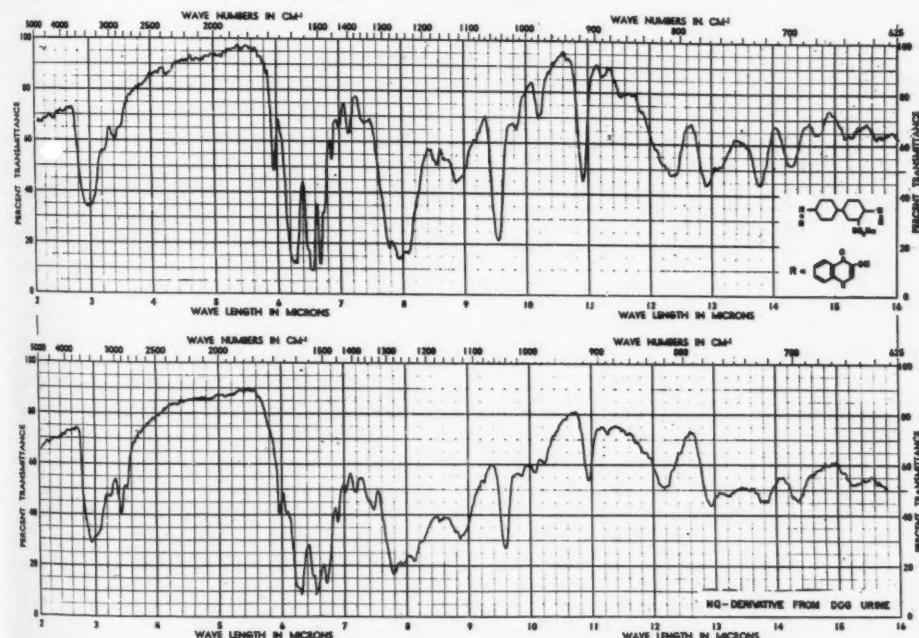


FIGURE 2. Comparison of infrared spectra of naphthoquinone derivative obtained from synthetic benzidine-3-sulfate with that obtained from dog urine.

urine did not, suggesting the presence of N-glucuronide in the rabbit urine.

SURVEY OF OTHER AMINES

A preliminary survey of the excretory pattern of a group of amines was carried out with the dog and rabbit. The compounds were administered intraperitoneally in water or water-alcohol. The compounds examined were aniline, α - and β -naphthylamine, methylene dianiline, orthodiamisidine, and 3,7-diaminodibenzo thiophene dioxide. The latter two were examined only in the dog. The procedure as described above for the estimation of ether-soluble and water-soluble aromatic amines was used. The water-soluble portion presumably represents the sum of glucuronide and sulfate esters.

The results are shown in Table II; benzidine is included for purposes of comparison. It can be seen that with these amines, as with benzidine, the portion of the injected dose found in the urine by the NQS technique is substantially lower with the rabbit than with the dog.

The ether extractable portion in dogs appeared higher than in rabbits. 3,3'-diorthoanisidine and 3,7-diaminodibenzo thiophene were almost completely recovered in the urine and it was possible to isolate the amine and show, by

infrared spectra, mixed melting point and paper chromatography, that the material was identical with injected compounds. Accordingly these two compounds appear not to be metabolized.

Discussion

The ortho hydroxy derivative of aromatic amine has been implicated as the direct agent responsible for bladder cancer.⁶ One of the reasons for this is the fact that only aromatic amines with the para position blocked have been found to be involved in the production of bladder cancer. Thus, aniline and 1-naphthylamine do not appear to cause bladder cancer in man, while benzidine and 2-naphthylamine do.⁷ Hydroxylation of the aromatic ring is the usual metabolic pattern ("detoxication") and the amino group is an ortho-para director, accordingly, ortho hydroxylation is to be anticipated when the position para to the amino group is blocked.

The view that the ortho hydroxy amine is indeed the carcinogen was strengthened by the observation that 2-amino-1-naphthol⁸ and the glucuronide of the compound produced tumors when inserted into the bladders of mice, while 2-naphthylamine and the sulfate ester of 2-amino-1-naphthol did not.⁹

TABLE II
Metabolites in % of Injected Dose

Compounds	Metabolites	Animals							
		Dog		Rabbit		Rabbit		Rabbit	
		24 hr	48 hr	24 hr	48 hr	24 hr	48 hr	24 hr	48 hr
Aniline (1 gm dog 500 mg rabbit)	Ether soluble amine	15.5	4.5	12.5	1.5	13	1.2	10	1.4
	Water soluble conjugates	43.0	13.2	22.7	6.6	23.6	6.4	19.2	5.2
	Total	58.5	17.7	35.2	8.1	36.6	7.6	29.2	6.6
	Total (48 hr)		76.2		43.3		44.2		35.8
Alpha-naphthylamine (500 mg dog 100 mg rabbit)	Ether soluble amine	14	4.9	5	3.5	6.2	3.2	4.3	4
	Water soluble conjugates	45.5	24.0	25.8	18.0	26.3	13	21.7	15.0
	Total	59.5	28.9	30.8	21.5	32.5	16.2	26.0	19
	Total (48 hr)		88.4		52.3		48.7		45
Beta-naphthylamine (1 gm dog 100 mg rabbit)	Ether soluble amine	36.3	0.7	20	2	22.3	2.4	24	2.8
	Water soluble conjugates	47.5	1.3	28	2.3	25.7	1.8	27	2.0
	Total	83.8	2	48	4.3	48	4.2	51	4.8
	Total (48 hr)		85.8		52.3		52.2		55.8
Benzidine (1 gm dog 100 mg rabbit)	Ether soluble amine	28	0.8	7.7	2	6	1.6	8	2.5
	Water soluble conjugates	56.1	1.6	20.5	5.0	29.0	3.0	27.1	5.8
	Total	84.1	2.2	28.2	7	35	4.6	35.1	8.3
	Total (48 hr)		86.3		35.2		39.6		43.4
Methylene-dianiline (1 gm dog 100 mg rabbit)	Ether soluble amine	19.6	0.5	2	0.2	2	0.5	3	0.4
	Water soluble conjugates	67.0	2	46.0	4.3	36.0	5.5	35.0	6.8
	Total	86.6	2.5	48	4.5	38	6	38	7.3
	Total (48 hr)		89.1		52.5		44		45.2

The work reported here demonstrates that the metabolites of benzidine result largely from ortho hydroxylation. In fact, the observation that 3,3'-diorthoanisidine was excreted unchanged by the dog suggests that ortho hydroxylation is the only type of chemical change this species can produce.

We failed, however, to find free, unesterified 3-hydroxybenzidine in dog urine, in general agreement with a similar failure to observe free 2-amino-1-naphthol in dogs receiving 2-naphthylamine.⁹ Despite a deliberate search and in agreement with Sciarini,¹⁰ we also have been unable to find any evidence for the 3,3'-dihydroxybenzidine reported by Baker.¹¹

While the glucuronide of 3-hydroxybenzidine which we did observe in dog urine may well be the carcinogenic agent as suggested by Boyland⁸ the occurrence of the same derivative in rabbit urine makes it difficult to explain the non-occurrence of bladder cancer in this species. In this connection the two differences reported here between the dog and rabbit metabolism of aromatic amines are of interest: (1) the ability to conjugate the amino groups shown by the rabbit but not by the dog, and (2) high proportion of ether extractable metabolites found in dog urine.

Summary

A method for the study of the urinary metabolites of aromatic amines has been developed based on the formation of a derivative with naphthoquinone sulfonate. This method aids in the identification of such metabolites and can be used quantitatively. It has been applied to the identification of urinary metabolites of benzidine in several species and to a preliminary survey of the metabolites of a group of carcinogenic and non-carcinogenic aromatic amines. The chief findings have been that the major metabolites of benzidine in the dog and rabbit appear to be the sulfate and glucuronide of 3-hydroxybenzidine. No unesterified hydroxy derivatives were found. It has not been possible to confirm an earlier report of a dihydroxy urinary me-

tabolite of benzidine. The excretion of amine metabolites in the rabbit and dog differed chiefly in the following three respects: (1) dogs excreted relatively more sulfate conjugate; (2) dogs excreted more than 80% of the dose in the form of compounds with an available aromatic amino group, while rodents excreted less than 50%, and (3) dog urines had a larger ether extractable amine fraction containing unidentified amine metabolites.

Acknowledgments

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2. Aided by a grant from the National Aniline Division of the Allied Chemical & Dye Corporation.

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The Pharmacological Effects of Magnesium Arsenate Phosphor upon Experimental Animals

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Introduction

MAGNESIUM arsenate, a luminescent chemical, shows a red fluorescence when excited by ultraviolet radiation. For this reason, the material has potential use as a color correction phosphor in high-pressure mercury vapor and fluorescent lamps and as a red phosphor in fluorescent sign tube manufacture. Although the material may be considered chemically as relatively insoluble, all arsenic compounds are to be looked upon with suspicion from the health and safety standpoint. Since operations employing the materials may involve dust exposures, it was felt that an evaluation of its toxicity should be made in its development program. Therefore, magnesium arsenate was tested to determine its pharmacological and toxicological properties in experimental animals.

Methods

Young adult, male and female Sprague-Dawley Holtzman strain rats (170 to 320 gm), Carworth Farms Swiss mice (15 to 40 gm), young adult albino rabbits (1.5 to 2.1 kg), and adult mongrel dogs (5.5 to 9.5 kg) were used for these experiments. The mice and rats were housed in air-conditioned rooms in which the temperature was 23° to 24°C and the relative humidity ranged from 52 to 56 per cent. The temperature in the dog and rabbit quarters varied from 27° to 29°C. All animals were allowed free access to food and water.

Magnesium arsenate phosphor is a white, amorphous solid which is practically insoluble in water, propylene glycol, alcohol, or other vehicles suitable for injection. It was administered to the animals as an aqueous suspension containing one per cent carboxymethylcellulose. There were no apparent toxic effects due to carboxymethylcellulose. After an animal was treated, it was kept under observation for 14 days. The approximate lethal dose (ALD) was determined by the method of Deichmann and

LeBlanc.¹ The sample of magnesium arsenate phosphor was supplied by Sylvania Electric Products, Inc. (1740 Broadway, New York, New York).

Results

ACUTE TOXICITY AND PHARMACOLOGICAL EFFECTS

From Table I it may be noted that the ALD of magnesium arsenate phosphor is 0.28 gm/kg for rats (P.O.), 2.1 gm/kg for rats (I.P.), 4.7 gm/kg for mice (P.O.), and 0.08 gm/kg for rabbits (P.O.).

The administration of a single oral dose to a rat, mouse or rabbit caused lethargy, anorexia, gastroenteritis, severe diarrhea with watery stools and loss of body weight. These effects occurred with oral doses of 0.18 gm/kg in the rat, 80 mg/kg in the rabbit, and 2.1 gm/kg in the mouse. Doses smaller than these produced few, if any, signs of intoxication. All rabbits and practically every rat that developed the diarrhea did not recover. These signs closely resemble those of arsenic poisoning, particularly the "rice water stools".

The diarrhea, apparently, was not due to mechanical irritation of the intestinal mucosa because of the delayed onset of the diarrhea. Even with extremely large doses (up to 36 gm/kg in the rat), 20 to 24 hours elapsed before these signs of intoxication were noted. This would indicate rather slow absorption from the gastroenteric tract, delayed action of the compound, or a combination of both. The survival time was also rather long (24 to 72 hours).

Doses approximately ten times those administered orally were required to cause signs of toxicity or death from intraperitoneal injection. The ALD (in the rat) by this route was 2.1 gm/kg. Little or no diarrhea was found after the administration of doses as high as 10.7 gm/kg and the survival time varied considerably from animal to animal, indicating that the rate of absorption from the peritoneal cavity was quite slow and erratic.

The instillation of one milliliter each of one, five and twenty per cent suspensions, respectively, of magnesium arsenate into one eye of a rabbit (other eye served as the control) caused little or no irritation. Dusting a small amount of the powder into the eye (rabbit) caused only slight irritation with congestion in the vessels of the cornea and conjunctiva.

The oral administration of magnesium arsenate to two dogs (0.17 and 0.184 gm/kg) caused nausea and vomiting. Each dose was administered four times to each dog, twice in capsules and twice mixed with canned horse meat. Following all four doses, each dog vomited profusely (35 to 45 minutes after administration in capsules and 60 to 75 minutes after administration with horse meat). Subsequently, they were hypoactive for about two hours, but this was probably due to the physical exertion of retching.

This compound was injected into three dogs intramuscularly (0.21, 0.268 and 0.308 gm/kg) and into two dogs subcutaneously (0.21 and 0.308 gm/kg). There was marked pain and irritation at the site of injection. The dogs appeared normal about four hours after subcutaneous injection. There was a hard area at the site of injection about eight or nine centimeters in diameter, indicating very slow absorption.

After an intramuscular injection, the dog limped or carried the injected limb off the floor for about 24 hours. The injected limb remained markedly swollen for several days and one dog developed a cutaneous ulcer at the site of injection.

These dogs were sacrificed by electroshock and examined post-mortem on the sixth day after injection.

Gross Pathological Changes: Post-mortem examination of animals killed by oral administration revealed hemorrhages and inflammation of the intestines and, with the larger doses, a sloughing of intestinal mucosa. The intestines were filled with a watery fluid and there were no formed stools in the colon.

Following I.P. injection into rats, the material was found in the peritoneal cavity, encapsulated like a foreign body.

Post-mortem examination of dogs which were sacrificed revealed that most of the compound was not absorbed, but still deposited and encapsulated at the site of subcutaneous injection. In the leg muscles, after an I.M. injection, it caused marked edema and tissue destruction. The compound was retained in the muscle with serosanguineous fluid and cellular debris.

TABLE I
Approximate Lethal Doses (ALD)
of Magnesium Arsenate Phosphor

Species	Route of administration	Number of animals	ALD mg/kg	Survival time hours
Rabbit.....	P.O.	6	0.08	18 to 72
Rat.....	P.O.	20	0.28	24 to 72
Mouse.....	P.O.	24	4.70	48 to 72
Rat.....	I.P.	39	2.10	24 to 144

SUBACUTE TOXICITY IN RATS

Effects on the Hematopoietic System of Rats: Twenty rats (ten males and ten females) were treated orally with the magnesium arsenate phosphor to determine the effects of multiple, sub-lethal doses. The arsenate was administered three times weekly in a dose of 0.14 gm/kg (one-half of the approximate lethal dose). Ten other rats (five males and five females) were selected to serve as controls. All rats were weighed three times a week.

Blood studies were conducted once a week using tail blood. Determinations included counts for total red blood cells, total and differential white blood cells, and circulating eosinophils, and determinations of hemoglobin and hematocrit.

From these data, it was concluded that the blood counts of treated rats were not significantly different from the counts of the control animals until about one month (12 doses or a total of 1.68 gm/kg) after the start of the administration of the compound. At this time the animals started showing signs of intoxication, such as anorexia, lassitude, enteritis, diarrhea and loss of body weight. Even then there were no significant changes in the total red cell count, hemoglobin, hematocrit, circulating eosinophils, total white cell counts and eosinophil, monocyte or basophil counts. There were, however, statistically significant changes in the numbers of circulating lymphocytes and neutrophils. The number of circulating lymphocytes (Figure 1) was decreased, while the number of circulating polymorphonuclear leukocytes (Figure 2) was increased. In most cases, there were gradual changes in the lymphocyte counts which occurred about five days before death. These changes were most marked 24 hours prior to death.

In Figures 1 and 2 the mean values of the total number of cells were plotted against time after the start of the administration of the compound.

Loss of Body Weight of Rats: In the acute experiments it was noted that the animals lost considerable body weight prior to death. This was well illustrated in the rat subacute studies previously described. In general, there was a normal increase in body weight for about four weeks, then the signs of intoxication became apparent. Concurrent with these signs was a progressive loss of body weight until death.

From the 31st to 38th day after the start of the experiment the control group of males showed an increase in mean body weight of nine grams while those treated with the arsenate showed a decrease in mean body weight of 50 grams. Likewise, the control females gained one gram (mean body weight) while the treated females lost 23 grams (mean body weight). The weight loss was probably due to a combination of anorexia and dehydration caused by severe diarrhea.

ANTAGONISTIC EFFECTS OF DIMERCAPROL:

Since the signs of intoxication caused by this compound very closely resembled those of acute arsenic poisoning, Dimercaprol (BAL) was injected into rats and rabbits to determine its antitodal effect.

Magnesium arsenate phosphor was administered in a single oral dose of 0.56 gm/kg (twice the approximate lethal oral dose) and BAL was injected intramuscularly at four hour intervals.

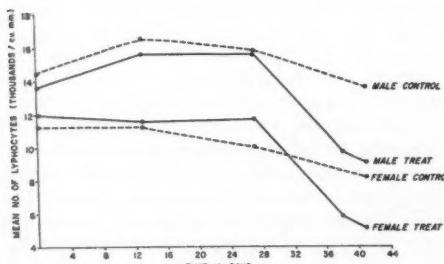


FIGURE 1. Effect of magnesium arsenate phosphor on lymphocytes in rat blood.

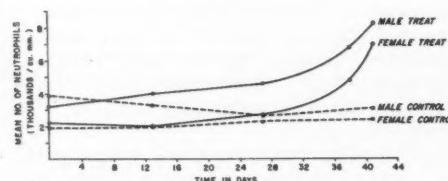


FIGURE 2. Effect of magnesium arsenate phosphor on neutrophils in rat blood.

TABLE II
Influence of Dimercaprol (BAL) on the Mortality of Magnesium Arsenate Phosphor (MAP) in Rats

Ten rats per group

Identification No. of group	MAP gm/kg	BAL mg/kg	No. doses of BAL	Per cent mortality
II	0.56	4	6	90
V	0.56	20	4	60
VIII	0.56	40	4	20
IX	0.56	60	4	0
I	0.56	—	—	80
IV	0.56	—	—	90
VII	0.56	—	—	100
III	—	4	6	0
VI	—	20	4	0
X	—	40	4	0
XII	—	60	4	0

TABLE III
Influence of Dimercaprol (BAL) on the Mortality of Magnesium Arsenate Phosphor (MAP) in Rabbits

No. of rabbits treated	MAP gm/kg	BAL mg/kg	No. doses of BAL	Fate of Animals	Survival time hours
4	0.16	4	6	All died	28 to 48
4	0.16	40	2	All died	15 to 18
2	0.16	60	2	All died	5 to 6
1	0.16	80	2	All died	8
4	0.16	—	—	All died	18 to 28
2	—	4	6	Survived	
2	—	40	2	Survived	
1	—	60	2	Survived	
1	—	80	2	All died	3 to 4

Ten rats were in each group (Table II). No protective effects were seen with BAL in doses of 4 and 20 mg/kg. It was found that 40 and 60 mg/kg doses of BAL did prevent death from a lethal dose of the arsenate. Repeated injections of BAL were needed to afford this protection. The injection of BAL did not, however, prevent some of the signs of intoxication due to the arsenate such as anorexia, lassitude, diarrhea and loss of body weight.

The antitodal effect of BAL was also tested in rabbits (Table III). In doses of 4, 40, 60, and 80 mg/kg, BAL did not prevent death from the orally administered arsenate. With the 4 mg/kg dose of BAL, the period of survival was increased. Also the onset of diarrhea was not as rapid, nor did it seem to be as severe as in the untreated rabbits; otherwise, no protective effects by BAL were demonstrated in the rabbit.

These results indicate that BAL prevents the lethal effects of magnesium arsenate in the rat, but not in the rabbit.

INFLUENCE OF ENVIRONMENTAL TEMPERATURE ON THE TOXICITY IN RATS

The results of certain experiments performed in this laboratory indicate that the environmental temperature influences the toxicity of various compounds. In a hot environment the compounds were more toxic to rats. The oral toxicity of magnesium arsenate phosphor in rats was tested under these conditions. The following are the environmental temperatures and approximate lethal oral doses for each group of ten rats.

Group I—Room Temperature 36°C 55 mg/kg

Group II—Room Temperature 27°C 280 mg/kg

Group III—Room Temperature 4°C 1400 mg/kg

From these data it was concluded that rats kept in a hot environment succumb to a much smaller dose of the arsenate than those kept at room temperature. Those kept in a cold room withstood much larger doses of the arsenate.

Summary and Conclusions

1. Magnesium arsenate phosphor administered orally to rats, mice and rabbits caused marked

irritation of the gastroenteric tract leading to anorexia, enteritis, diarrhea, loss of body weight and death. In dogs this irritation caused vomiting to such an extent that a lethal dose was not retained.

2. This compound was poorly absorbed from parenteral sites of injection. Intraperitoneal injections into rats caused death, but at a dose much higher than the lethal oral dose. Subcutaneous and intramuscular injection into dogs caused local irritation and tissue damage.

3. Repeated subacute doses (orally to rats three times weekly) caused loss of body weight, lymphocytopenia, neutrophilia and death.

4. Dimercaprol (BAL) prevented death from the oral administration of this compound in rats, but not in rabbits.

5. In a hot environment rats succumbed to much smaller doses of the compound than those kept at room temperature. Rats kept in a cold room withstood much larger doses than those kept at room temperature.

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SPECTROGRAPHERS' MEETING

THE TENTH Annual Symposium on Spectroscopy of the American Association of Spectrographers is to be held at the Conrad Hilton Hotel in Chicago, Illinois from June 1 through June 4, 1959. Original papers in the fields of emmission, x-ray, visible, ultraviolet, near-infrared, Raman spectrometry, and flame photometry will be offered. The meeting will also feature an instrument exhibit.

LIBRARY LIST

AVAILABLE is a new *Union List of Scientific and Technical Publications of the Libraries of Cincinnati and Vicinity*, sponsored by the Cincinnati Chapter of Special Libraries Association, compiled and edited by Gertrude Bloomer, assisted by Dottie F. Broft and Irene Campbell. It covers the holdings of 35 libraries to January 1958. Orders for copies of this list should be sent to the business manager: Roberta Andrews, Librarian, U.S.P.H.S., Occupational Health Field Headquarters, 1014 Broadway, Cincinnati 2, Ohio. Cost per copy \$10.00.

Chemical Constitution and the Toxic Action of Narcosis*†

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CERTAINLY this audience needs no reminder of the complex problems involved in determining the toxicity of chemical compounds. In 1949, Dr. Smyth¹ stated, "One chemist can in a year make enough chemicals to occupy the full attention of one toxicologist for a lifetime". This statement is surely more than ever true today.

For this as well as for more fundamental scientific reasons, it has been a natural consequence for the toxicologist to look for relationships between chemicals which might be useful in foretelling some toxic effect. One obvious relationship would involve the constitution, or the structure and properties, of chemicals. Probably many here are familiar with the relation between chemical structure and color. Chemists have for many years known of the types of structure which result in color and of the structure changes which inhibit or intensify color. While there are no direct analogies in biological areas, there is a vast amount of literature about the relationships between chemical constitution and biological activity. This information has for the most part come from pharmaceutical laboratories. Important chemicals or drugs such as aspirin, the sulfonamides, DDT, novocaine and many others have developed through knowledge of structure activity relationships and the intelligent attempt to design a suitable biologically-active molecule.

The prime example is undoubtedly the barbiturate drugs.² Over 2500 barbiturates have been prepared. Figure 1 shows the general structural formula for the barbiturates. Barbiturates are useful for their sleep-producing or hypnotic properties. Briefly summarized, it may be said that both R-1 and R-2 must be alkyl or aryl groups in order for the compound to have any hypnotic properties. The hypnotic potency increases until there is a total of about eight carbon atoms on R-1 and R-2, after which potency declines and convulsant properties appear. Alkyl groups at R-3 are characterized by en-

hanced potency and relatively short duration of action. However, if both nitrogen atoms have alkyl groups there is a tendency to produce convulsions. If X, which is normally an oxygen atom, is replaced by sulfur, the duration of action is short. Thus, it is possible to design molecules with a large variety of different potencies and variations in duration of action.

These are, of course, generalizations for a specific basic molecule. Changes made in one molecule are not necessarily useful for predicting changes in another molecule. Some compounds will lose their activity if the slightest change is made and in many cases optical isomers differ widely in biological activity.

In the field of toxicology, if we are to describe the relationship between chemical structure and toxicity we must keep in mind that toxicity or toxic action may imply more than a single specific physiological action. For example, if the effects of a hypothetical chemical are plotted against dose, as in Figure 2, we might suggest toxic action at many different sites, such as the central nervous system, the blood, the kidney, or the lung. The toxic action noted would vary considerably depending on the criteria of observation. It is important then that when we speak of relationships of structure and activity in toxicology we must have in mind a toxic action which is a defined specific physiological or biochemical function. For example, a study of the organophosphorus compounds may relate structure to the pupil-constricting action or the inhibition of cholinesterase enzyme by these chemicals.

The most voluminous writings on these chemical composition-toxicity relationships have been by Von Oettingen in the Public Health Bulletins. These reports include extensive literature surveys but, by and large, they offer little in regard to interpretation and evaluation. Perhaps at this time the state of knowledge does not warrant any attempts to interpret. Perhaps the more important task at the present is to collect pertinent data, withholding interpretation until greater insight is available. Perhaps the present information is too incongruous to be used for

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† This investigation was supported in part by research grant RG-4799 from the Division of Research Grants, National Institutes of Health, U. S. Public Health Service, Bethesda, Maryland.

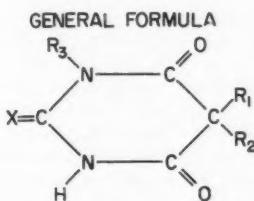
**Barbiturates**

FIGURE 1.

meaningful relationships. The late Dr. Fairhall concludes a discussion with these words, "It will be apparent therefore that while the temptation to rationalize regarding the prediction of toxicities may be great, the evaluation of toxicities of new substances is fraught with considerable uncertainty. Since no great rationale scheme is available to aid, except rather sketchily, in deciding upon the toxicity of a given substance, it is inevitably necessary to carry out experimental work with animals".

I would like to emphasize two factors which appear to me to be stumbling blocks in considerations of structure-activity relationships. The first of these is the question of replacement of animal experiments. Animal studies will without a doubt be with us for many, many years, so that an equally important goal of structure-activity studies, is not the replacement, but the more intelligent and expeditious use of experimental animals. The second factor is the attempt to compare the same structure change in grossly different molecules. To illustrate such a comparison consider two examples of change in toxicity effects with the addition of a methyl group. Resorcinol is less toxic than dimethyl resorcinol, but methyl dichloroarsine is more toxic than dimethylchloroarsine. Such comparisons only seem to cloud the issue. No mention is made of the gross difference in molecules or the simultaneous change in chlorine atoms. There are enough anomalies without reaching for the extremes.

The most extensively studied compounds in regard to biological activity are unique in that they bear no rigid structural resemblance to one another. Their common factor is that they all produce the physiological action of narcosis. These compounds include hydrocarbons, alcohols, ketones, esters and other compounds classified as hypnotics, narcotics and general anesthetics.

Before proceeding I should define what I mean by narcosis, since there is a wide discrepancy in its use. In legal usage a narcotic refers to an

addictive drug. However, in pharmacology, a narcotic, or narcosis-producing chemical, generally refers to a depression of the central nervous system which is reversible in action. For practical purposes I like to use the description by Dr. Smyth,³ which gives a working definition of narcosis as impaired coordination, through dizziness, to anesthesia.

It was observed many years ago that these chemicals which produce narcosis, have certain physicochemical properties in common. For example, solubility in oils is the basis for the well-known Meyer-Overton theory.⁴ Table I shows a series of compounds which have produced narcosis in tadpoles. The concentration of the chemical in the water surrounding the tadpole is given in terms of moles per liter times 100 and it is seen to vary by a factor of 7000. If this water solution was in equilibrium with some oil, the concentration in the oil, also in terms of moles per liter times 100, is shown and is seen to have only a variation of 2.5 times.

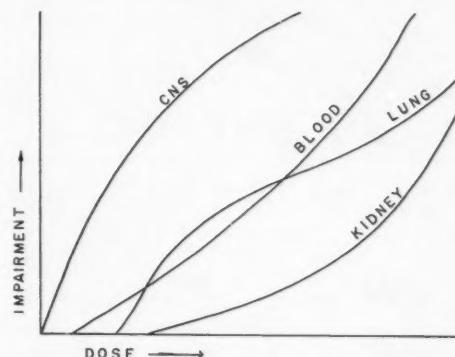


FIGURE 2.

TABLE I
Narcosis in Tadpoles
(Meyer, 1937)

	Concentration	
	In water	In oil
Ethyl alcohol.....	33.	3.3
Butyl alcohol.....	3.	2.0
Ether.....	2.4	5.0
Salicylamide.....	0.33	2.1
Carbon disulfide.....	0.05	3.0
Chloroform.....	0.008	2.6
Thymol.....	0.0047	4.5
Range.....	7000 fold	2.5 fold

TABLE II
Narcosis in Mice
(Meyer, 1937)

	Concentration	
	In air	In oil
Methane.....	370.	8
Nitrous oxide.....	100.	6
Acetylene.....	56.	5
Ethyl chloride.....	5.	7
Ether.....	3.4	9
Carbon tetrachloride.....	0.6	7
Chloroform.....	0.5	9
Range.....	740 fold	1.8 fold

Similarly, Table II shows a series of chemicals producing narcosis in mice. The air concentration, in volumes per cent, varies 740 times and the oil concentration, in moles per liter times 100, varies only 1.8 times. In addition to oil solubility, studies have been reported^{2, 5} supporting theories which involve surface tension, permeability, coagulation, flocculation, adsorption and electric action potential.

These theories based on physical properties were not satisfactory for the biochemists and pharmacologists who were interested in the mechanism of chemical reaction which results in narcosis. When experimentation with enzymes came into vogue, studies were made based on the observation that these chemicals interfered with the use of oxygen by the cell. Efforts were made to find an enzyme or system which was specifically inhibited by narcotics. This seems logical since physiological facts indicate a very high degree of dependence of the central nervous system on the maintenance of oxygen and glucose supply. However, extensive experiments on aerobic and anaerobic glycolysis did not result in a site of action to explain the inhibition of narcotics. It was then thought that the interference with oxygen consumption might be secondary to a depression of the formation of high

energy phosphate bonds. These phosphate bonds provide the necessary energy for biological reactions. The results obtained have not been widely applicable. Biochemical studies have delved further and further with each experiment often raising more questions than it answered. Suffice it to say that at the present time we have no acceptable mechanism of action to explain narcosis. It might be well to keep in mind that it is not a foregone conclusion that all narcotics must act by the exact same mechanism.

The fact that theories of physicochemical properties have not aided much in detailed mechanism studies, does not necessarily mean that they are incompatible with regard to the overall mechanism of narcosis. For example, in Figure 3 consider the physicochemical properties as being rate-determining as in A to B. That is, this step controls the amount of drug reaching the active site. This does not prevent the actual effect or toxic mechanism from being due to complex enzyme reactions.

Ferguson⁶ introduced some new ideas into the theories based on physicochemical properties. He recognized that when we compare toxicities of compounds, instead of using the external concentration, it is usually more proper to compare the internal concentration at the site of toxic action in a man, a cell, or whatever system is used. This internal concentration is, unfortunately, almost never known. Ferguson then proceeded to make use of the assumption that there are some chemicals which establish an equilibrium between the external and internal concentration.

To examine this equilibrium we will consider three immiscible liquids. Figure 4 represents these liquids as phases A, B, and C. If some compound X is added, it will distribute itself between the three liquids. After a certain time, compound X will dissolve in each liquid and reach an equilibrium concentration which we have indicated with the small letter subscripts as X_a , X_b , and X_c . There is also some concentration which represents the maximum amount of X soluble in each liquid. This is the saturated concentration indicated with the capital subscript as X_A , X_B , and X_C .

Let us assume some arbitrary numerical values for these saturated concentrations, $X_A = 10$; $X_B = 100$; and $X_C = 50$. We see then that X is ten times more soluble in liquid B than in liquid A. Physical laws tell us that at equilibrium we will expect that liquid B contains ten times the amount of X in liquid A. Similarly, since $X_B = 100$ and $X_C = 50$, we will expect to find twice as much of X in liquid B as in liquid C.

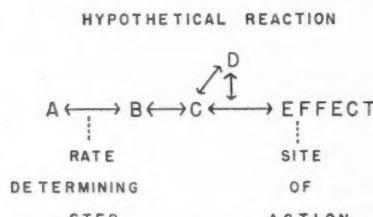
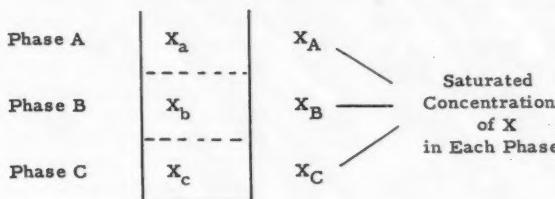


FIGURE 3.

EQUILIBRIUM BETWEEN PHASES



$$x_a/x_A = x_b/x_B = x_c/x_C$$

FIGURE 4.

Now if we had added sixteen units of our concentration to this system, we would then expect to find, at equilibrium, one unit in A, ten units in B, and five units in C. This is the same ratio of concentrations as the saturated concentrations, 10, 100, and 50. It is obvious, then, that the ratio of the concentration in the liquid to the saturated concentration, which is 1:10 in A, 10:100 in B, and 5:50 in C, is identical in each liquid, being one-tenth numerically. This means that if we have an equilibrium system in which information about phase C is completely unknown, we may still know the ratio X_c/X_0 from information about phase A.

This example is a simplification and approximation of a more exact physicochemical statement developed by G. N. Lewis⁷ which says that in an equilibrium system the partial molal free energy in each phase must be the same. With due apologies to the physical chemists here, I will use the concentration ratio as described and will refer to it as the Ferguson Value. If one of the phases is air rather than a liquid, its Ferguson Value is calculated from the vapor pressure of the chemical in the air divided by the saturated vapor pressure of the chemical.

If X is a compound which produces narcosis, if phase A is the external phase and phase C is the internal site of toxic action, then although we do not know the internal concentration, we do know the Ferguson Value which is calculated from the external concentration. Albert⁸ has expressed the Ferguson concept as, "substances which are present at the same proportional saturation in a given medium have the same degree of biological action". In summary, the following developments should be noted: (1) that there is a group of chemicals which act in a "physical" sense, allowing an equilibrium to be established; (2) that for these chemicals, the toxic effect at the site of action is produced by a fraction of the

saturation concentration at this site; (3) that this fraction is a constant for all chemicals falling into this category; (4) that this fraction, or the ratio $C(\text{tox.})/C(\text{sat.})$, cannot be determined at the site of toxic action; and (5) that it follows from thermodynamic theory that under equilibrium conditions the ratio at the site of toxic action is the same as the ratio in the outer environment. Since it is possible to measure the ratio $C(\text{tox.})/C(\text{sat.})$ in the external environment, it is possible to compare the toxic effect of different chemicals with this ratio.

Table III shows the Ferguson Value, calculated from the data shown in Table II, which produces narcosis in mice. It is seen that, like the concentration in oil, this value lies within a relatively restricted range. Ferguson reasons that the physicochemical theories, such as that of Meyer and Overton, are valid to the extent that they are consistent with the physicochemical laws of equilibrium distribution.

This concept should hold then for any system which is in true equilibrium and in which equilibrium is rate-determining for the toxic action. It may be observed that these conditions do not restrict the toxic action to narcosis. If some other effect is also secondary to the equilibrium conditions, it should be amenable to the concept. This has been found to be true for many diverse

TABLE III
Narcosis in Mice

Compound	Ferguson Value
Nitrous oxide.....	0.01
Acetylene.....	0.01
Ethyl chloride.....	0.02
Ether.....	0.03
Carbon tetrachloride.....	0.02
Chloroform.....	0.01

TABLE IV
Insect Toxicity
(Tattersfield and Roberts, 1920)

Compound	Toxic Concentration	Ferguson Value
Monomethylaniline.....	3.7	0.3
Pyridine.....	76.	0.1
Monochlortoluene.....	120.	0.9
Chlorbenzene.....	200.	0.5
Benzene.....	775.	0.2
Chloroform.....	1040.	0.2
Trichlorethylene.....	1200.	0.4
Pentane.....	16600.	0.9

TABLE V
Insect Toxicity
(Tattersfield and Roberts, 1920)

Compound	Toxic Concentration	Ferguson Value
Chlorpierin.....	2.	0.003
Hydrocyanic acid.....	20.	0.0007
Ammonia.....	23.	0.00008
Monomethylamine.....	24.	0.0023
Dimethylamine.....	22.	0.00035
Ethylamine.....	22.	0.004

biological systems, such as the inhibition of development of sea urchin's eggs, bactericidal concentrations for many organisms and the hemolysis of blood. Ferguson made calculations from the data of Tattersfield and Roberts for a series of organic chemical vapors which are toxic to insects. Table IV shows some selected compounds whose toxic concentration varies about four thousand times, but whose Ferguson Value is within a factor of ten. Table V includes compounds which are not considered to have any narcotic action and their Ferguson Value is seen to be of an entirely different order of magnitude than the 0.1 to 0.9 seen in Table IV. The Ferguson Value, although constant for a given set of compounds, will vary from one biological system to another. It will also vary depending on the criteria of measurement. Thus, in the case of narcosis of mice, the value was about 0.02, while in the case of insect toxicity it was about 0.5.

I would like to refer briefly to the work of McGowan⁹ who extended Ferguson's concepts in several ways. For example instead of using an experimental value for the saturated concentrations, McGowan used theory to predict the value. He used data such as polarizability and parachor for these predictions. Also he expresses what would be a Ferguson Value in logarithmic terms. This tends to minimize the difference be-

tween values. McGowan also developed a formula based on experimental data of Carpenter, Smyth and Pozzani. By mathematically manipulating these data, he was able to obtain a numerical factor for a given change in structure.

McGowan then proceeded to use his formulas to calculate MAC values. He did this despite recognizing that many MAC values are set on bases other than toxic effect. Actually McGowan's calculations are extrapolations down to some arbitrarily selected low level. This low level might conceivably indicate some minimal reversible narcotic effect. However, if one attempts to estimate a concentration near the MAC which would produce a given narcotic effect, McGowan's predictions agree within a factor of two less than 50 per cent of the time. Our feelings are that McGowan's equations are oversimplified and that more information is needed before they are to be useful. At the present time the Ferguson Value appears to give more meaningful information.

In the tables of toxicity data given by Dr. Smyth³ in the Cummings Memorial Lecture two years ago, 57 chemicals are listed whose most serious effect of inhalation is narcosis. An additional 23 chemicals have some degree of narcotic effect within ten times the MAC concentration. This is 80 out of some 215 chemicals with MAC values or about 37 per cent of the

TABLE VI
Inhibition of Growth
(Yeast Studies)

Compound	Ferguson Value
Methyl alcohol.....	0.07
Ethyl alcohol.....	0.07
Methyl "Cellosolve"	0.09
n-Propyl alcohol.....	0.04
iso-Propyl alcohol.....	0.03
1,4-Dioxane.....	0.04
n-Butyl alcohol.....	0.05
Aniline.....	0.06

TABLE VII
Inhibition of Respiration
(Yeast Studies)

Compound	Ferguson Value
Methyl alcohol.....	0.17
Ethyl alcohol.....	0.18
iso-Propyl alcohol.....	0.12
Acetone.....	0.11
Aniline.....	0.17

total. This is a sizable fraction and places narcosis in a very important position for study and consideration in toxicology.

If one attempts to study these chemicals by evaluating data from the literature, he often runs into problems such as unknown purity of the chemicals, ill-defined experimental conditions, and inability to coordinate results from different laboratories. Our laboratory is in the process of evaluating Ferguson's concept by studying the effect of chemicals on yeast cells. Under as carefully as possible controlled conditions, we are determining the Ferguson Value for a series of chemicals.

To be a useful tool our yeast studies should show the majority of these 80 chemicals from the MAC tables to have similar Ferguson Values. Table VI shows some selected chemicals having similar Ferguson Values calculated from growth inhibition studies. These values are calculated from the concentrations of each chemical observed to cause a 50 per cent reduction in growth relative to a normally growing yeast control. Table VII shows Ferguson Values calculated from inhibition of respiration by yeast. The concentration of chemicals which will reduce the volume of oxygen consumed by yeast in a glucose medium is observed, again relative to a normal control. The respiration studies are made by Warburg techniques and represent selected values from our data. A later report at the completion of our studies will describe our experimental techniques and will discuss the agreement of our results with those expected on the basis of Ferguson's concept.

At the present time we can say that there is good correlation insofar as predicting an expected narcotic effect, but information is lacking for evaluation of prediction on a quantitative basis. An example of the considerations involved is the case of aniline. Concern in aniline poisoning is largely with cyanosis due to methemoglobinemia. This effect overshadows any apparent narcotic effect. However, some animal experiments have indicated narcosis due to exposure to aniline. In the yeast system there is, of course, no hemoglobin, and apparently aniline behaves similarly to other narcotics.

Several obvious limitations must be recognized. Such a system will not necessarily give a rigid classification of all compounds useful as narcotics. It will not account for other toxic effects in the body which overshadow narcosis. It will not account for unpredictable peculiarities in metabolic alterations and storage. It will not account for extreme deviations from physico-

chemical laws that might be caused by ionization or mutual solubility of phases.

In summary we must state that any practical application by the industrial toxicologist should understandably be limited and guarded. With intelligent use, Ferguson's concept should be useful for predicting the likelihood of a chemical causing a narcotic effect. That is, by a relatively simple test such as on yeast, the toxicologist may determine if the chemical is similar to known narcotic chemicals. If so, there is a likelihood that the chemical will produce narcosis in more complex systems such as animals and man. This prediction is limited by effects, as indicated earlier, which are not related to a yeast cell. Whether or not such information is worth the effort to the toxicologist in planning his animal experiments may be debatable and of personal preference. However, we might look at this recognition of the role played by the chemical in reaching the site of toxic action as an inroad towards putting some system into a grossly complex problem.

In conclusion I would like to make several general observations regarding chemical composition and toxicity relationships. It would appear that studies in this area must be advantageous to the future of toxicology. However, because of the poor initial returns many laboratories are not able to devote time to such efforts. Also it appears likely that studies which are made do not get into the open literature because of their limited or negative nature. It is suggested that there is a dire need for communication between toxicologists as to the desirability and direction of such studies.

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Reduction of Air Flow Noises*

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IN ORDER to use air for industrial purposes, it must flow, and air flow can produce noise in a variety of ways. The noise thus generated is of prime importance to industrial hygiene personnel who are responsible for hearing conservation programs because many air flow noises have high energy levels at frequencies which are damaging to the ear.

One may classify air flow noises according to the velocity of air flow, or more practically, with the pressure of the air producing them. At atmospheric or low pressures, the rates of flow are low and are produced by such things as fans, blowers, and ventilating systems. High rates of flow are generally associated with air at high pressures—as for example, compressed air.

Air flow may be either laminar or turbulent, depending on the rate of such flow. In laminar flow, as the name suggests, the air stream moves in such a manner that each small increment of the air moves in a path parallel to its neighbors and in the direction of the main stream flow. The noise generated by this type of flow is so low in intensity as to be of no consequence as a noise hazard.

Turbulent flow, however, is characterized by irregularity and randomness entering into the flow path of the stream. When a fluid such as air undergoes rapid changes in the direction of its flow, small fluctuations of pressure occur within the fluid. These fluctuations of pressure in the fluid actually constitute what is defined as a sound wave.

Turbulence in itself is not noise, but can give rise to noise by such things as interaction with rigid surfaces, forced oscillation of duct walls, or even radiation of wave fronts, which produce sound.

Noise generated by turbulent flow may be at discrete frequencies, or a continuous noise spectrum, or a combination of both. At low flow velocities, discrete frequencies may be produced by such phenomena as a given number of fan blades per unit time cutting a flow stream, thus generating a tone at that frequency or its harmonics. Discrete frequencies can also be

caused by mechanical unbalance of rotating machinery which will cause transmitted vibration at the frequency of rotation. Turbulence interacting with duct walls capable of undamped resonances can also produce this result.

In high air pressure applications resulting in high velocity flow systems, discrete frequencies are most generally produced by the shedding of vortices where there is an obstruction in the path of flow. The frequencies thus generated are usually in the upper audible ranges and are known as Strudhal Frequencies.

Generation of continuous noise spectra, on the other hand, is almost always due to turbulence in the air flow itself. In this respect, it is interesting to note that the intensity of the noise generated varies between the fifth to eighth power of the flow velocity producing it, and therefore decreasing the velocity by one-half may reduce the noise by as much as 15 to 24 decibels.

One of the most widely used industrial applications of compressed air is to let it issue from a nozzle for cleaning purposes or the ejection of small parts. An unwelcome side reaction of such an arrangement is the production of noise. A characteristic of such noises, which is of extreme importance as far as damage to the ear is concerned, is the fact that they generally exhibit a spectrum with a great deal of energy in the higher frequencies.

Figure 1 shows the relationship of typical airflow noise and a suggested hearing loss-risk criteria curve. The tentative criterion is shown as a dotted line and is plotted as a series of allowable sound pressure levels in each of eight octave bands of frequencies. Thus the sound energy represented by the area between the curves to the right of their point of intersection, is the energy which is above a proposed limit with regard to damage to the ear.

At Liberty Mutual, Cudworth¹ and others have shown that by proper design, nozzle noise may be attenuated considerably. However, we have found that in the practical application of such nozzles, as for example, in the removal of parts from a punch press, the noise produced by the air escaping from the orifice of the nozzle usually is of secondary importance. This results from the fact that when air is directed against a

* Presented at the American Industrial Hygiene Association annual meeting on April 25, 1958, Atlantic City, New Jersey.

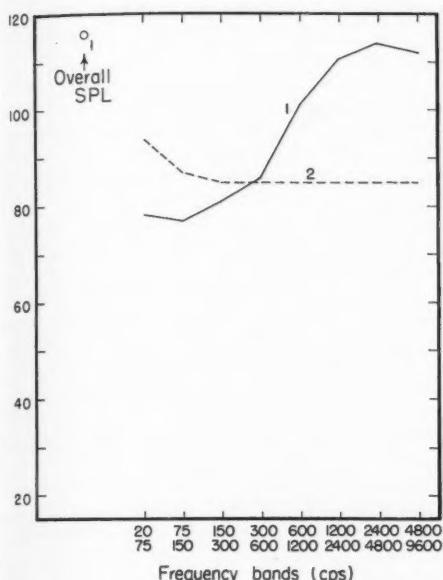


FIGURE 1. Sound levels in db (re: 0.0002 microbar) of air noise (solid line) versus a suggested hearing loss risk criterion (dotted line).

target, a noise of a much higher level than the nozzle noise is produced. The noise so produced is a function of the particular target set-up rather than a function of the nozzle design.

A series of tests were carried out to explore this point. In these experiments, the noise produced by nozzles of various designs was measured under a variety of conditions.

The table, Figure 2, gives some of the physical characteristics of a series of nozzles. The first four nozzles are a family of nozzles all of circular cross section and increasing in diameter in one-sixteenth inch steps. The last two nozzles are slot nozzles.

The noise produced by this series of nozzles discharging air at various line pressures directly into the atmosphere is given in Figure 3. It should be noted that the noise produced is not a simple linear function of the air pressure. This is important practically in that even small reductions in air pressure may make a worthwhile gain in noise attenuation. It can also be seen that when the nozzle design is held constant, the noise bears a direct relationship to the area of the nozzle opening and thus to the volume of the air being discharged.

Note, however, that when the shape of the nozzle is changed, the area may not be the determining factor. Nozzle E with a greater noise

NOZZLE CHARACTERISTICS

Nozzle	Shape of Cross Section	Area in Sq In.	Relative Area	Perimeter in In.	Relative Perimeter
A		0.01227	1	.392	1
B		0.02761	2.25	.59	1.5
C		0.04909	4.0	.785	2.0
D		0.0767	6.25	.98	2.5
E		0.1073	8.75	1.892	4.8
F		0.1510	12.4	3.0	7.66

FIGURE 2. Nozzle characteristics.

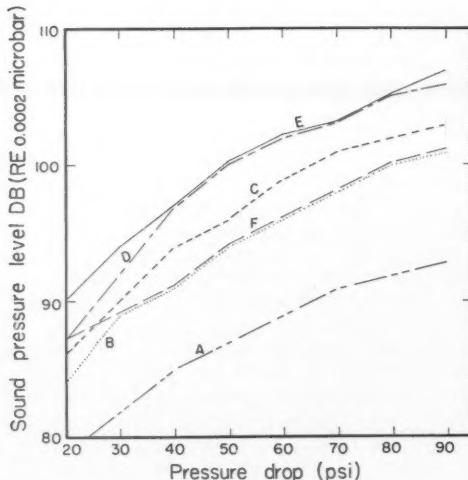


FIGURE 3. Sound levels of various nozzles. (See Figure 2 for description of nozzles corresponding to lettered curves.)

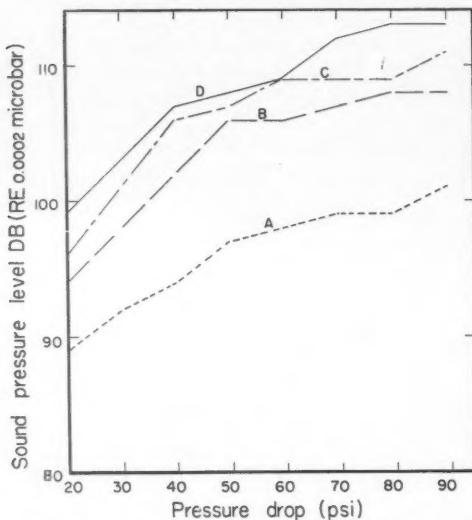


FIGURE 4. Sound levels generated by nozzles of circular cross section, with steel block target.

output is actually smaller in cross-section than nozzle F.

Figure 4 shows the results of impinging the discharge from these same nozzles against a target. It can be seen that for the same nozzle at the same pressure, the intensity of the noise has risen markedly. The increase is, in fact, so

large that the original noise would be no longer considered a contributing factor to the overall noise environment.

The target in this case is a sharp-edged block of steel and is used to illustrate the fact that when the flow of a fluid such as air undergoes a rapid change in direction, or when it impinges upon a sharp edge, turbulence and rapid pressure fluctuation are established, both of which phenomena produce noise. That this is a function of the target set-up is shown by a comparison of Figures 4 and 5.

All the conditions of the last set-up have been kept the same, with only the target being changed from the sharp-edged block to a screen of 1/16th inch mesh. It can be seen that the noise produced has been reduced markedly.

It has been established that the impingement of the nozzle output against the part to be removed from the press is of greater importance than nozzle design itself. In such a situation, attenuation of the noise produced may be achieved by slight changes in nozzle location, or even by incorporation of the nozzle into the die itself.

Any one of four commercially obtainable competitive mufflers reduced the overall noise level from 118 db to approximately 82 db. In cases where a muffler can be so used, this is a very worthwhile reduction in noise level.

The noise produced by air ejection may also be reduced by lowering the pressure of the air used to eject the part, and it has been shown that even slight changes in lowering the air pressure can reduce the noise produced. The noise reduction derived by thus lowering the air pressure must, however, be balanced against the economic risk of lowering the air pressure to such a point that non-removal of the part occurs with its attendant damage to the die. This is an economic decision which must be made separately for each case in question by the people involved.

Let us now look at a practical example of the reduction of the noise produced by a nozzle used to eject parts on a punch press which blanks out the end pieces for film reels. Figure 6, shows the results of sound measurements made before and after noise reduction alterations were made on the press. These alterations consisted of tilting the press approximately 35 degrees from the vertical plane, reducing the air pressure used to eject parts, and changing the air from continuous to intermittent operation. Tilting the press permitted the air pressure used to eject parts to be reduced considerably as the parts

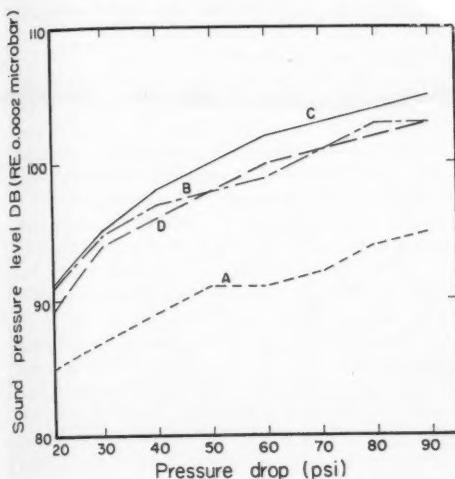


FIGURE 5. Sound levels generated by nozzles of circular cross section, with mesh screen target.

now tend to fall out of the machine by the pull of gravity.

The air used to eject parts was changed from a continuous stream which struck the die each time it entered its path to intermittent blasts which occurred only when the die was raised. These alterations reduced the overall sound pressure level at the operator's ear 11 db, which was found in the 4800-9600 cps band. It is interesting to note that, although these alterations were successful in reducing the noise of this press, the operator complained that after ten minutes of operation with the punch press in the inclined position, his back hurt to such an extent that he could not operate the press.

So far we have been primarily concerned with noise levels produced by high rates of air flow.

When we consider noises produced by medium or low flow rates, we find we must consider them in relation to a different type of criteria. These are the NC curves first suggested by Professor Beranek of M.I.T.²

Figure 7 illustrates one of a family of such curves. This one is NC-55, which is considered as the highest noise level acceptable in large office areas. Also plotted on this figure is an octave band frequency analysis of noise produced by a nozzle. The area between the curves to the right of the intercept represents the amount of noise reduction required to reduce this noise to an acceptable level in an area for office use.

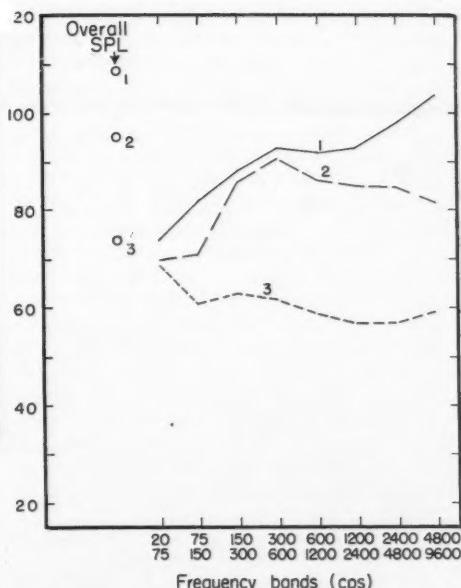


FIGURE 6. Sound levels generated by a blower press (SPL in db re: 0.0002 microbar). (1) Before alterations. (2) After alterations. (3) Background.

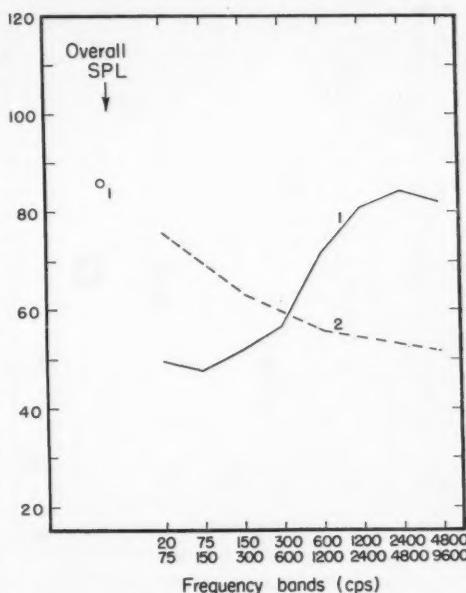


FIGURE 7. Sound level in db (re: 0.0002 microbar (solid line)) versus a suggested annoyance criterion curve (dotted line).

As an example of the reduction of a noise level produced by medium rates of air flow we shall consider a dryer, which was essentially a perforated plate through which air was impinged upon material carried on a belt, and which produced a noise spectrum which had most of its energy in the 1200-2400 cps band and was extremely annoying. The noise did not reach this level on the dryer as originally installed, but rose to this level upon the installation of a new belt as a maintenance procedure. It was found that absorption batts in the dryer plenum above the perforated plates would cause complete cessation of the noise. The batts absorbed enough sound energy to destroy the standing wave pattern which was set up at the plenum chamber's natural resonant frequency. They were objectionable from a machine-cleaning standpoint, however; and the final solution consisted of chamfering the up-stream end of all the holes. This brought the noise down to background conditions in the room.

A different type of situation is shown in Figure 8 which is an example of a neighborhood annoyance problem. The measurements shown are the before and after conditions in a residential section a thousand feet away from a steam exhaust which was the source of noise. This re-

duction was accomplished by the installation of a commercially obtainable muffler.

When one thinks of examples of low flow rate noises which may be of interest to industrial hygienists, ventilating system noises immediately come to mind.

Modern ventilating systems are comprised of a whole host of components that may contribute to the noise output of such systems. The fans and blowers, in addition to moving the air, generate noise in various ways. Since in all practical duct systems the air flow velocity is high enough to produce turbulent flow, the generation of noise can be expected.

Noises reaching a worker through ventilating systems may be of two kinds: that is, noise brought into the room through the ducts, and noise transmitted through the building construction itself. Since we are here concerned with air flow noises, in the interest of brevity, we shall limit ourselves to the consideration of only the noises carried through ducts.

Duct borne noise falls into two categories— aerodynamic and non-aerodynamic. Aerodynamic noise arising from ventilating fans may be divided into the noise caused by rotation of the fan and that due to vortex shedding. Rotational noise is generally a series of pulses of such a frequency, or harmonics of such frequency, as to bear a definite relation of fan rpm and number of fan blades. The noise caused by vortex shedding is random in nature having a broad spectrum. Non-aerodynamic noise may result from a great variety of causes, and does not fall into the category of air flow noise.

However the noises are produced, it is in the province of the industrial hygienist to measure such noises to see if they exceed the criteria. The general approach to sound control is to visualize noise control problems as composed of three parts: (1) the source, (2) the path from source to receiver, and (3) the receiver.

The reduction of ventilation noises then becomes the application of preventative measures to each of these parts.

Reduction of such noise can be accomplished by taking advantage of the fact that it is dependent on the flow velocity of the air in the system. Ducts may be lined or coated to eliminate duct radiation. Noise carried by the ducts themselves may be attenuated by the installation of sound-absorbing sections in the ducts, or by the lining of bends in the ducts, or the inclusion of lined or baffled plenums in the system. The kind and location of grilles can be changed to affect the noise generated by them. The room itself can be altered by manipulation

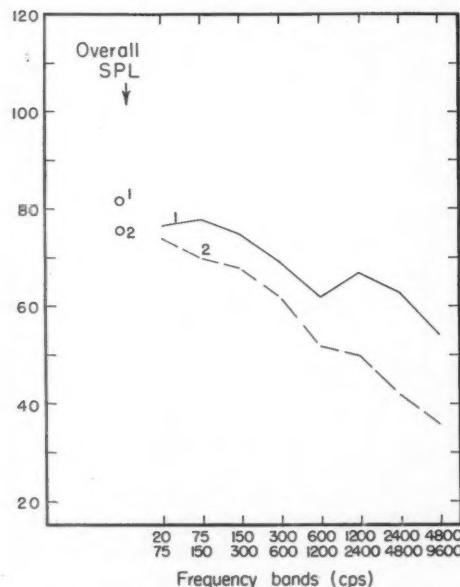


FIGURE 8. Sound levels in db (re: 0.0002 microbar) produced by a steam exhaust. (1) No muffler. (2) With muffler.

of its absorption to reduce the sound pressure level within it.

Not all the noise produced by ventilation systems is unwanted, however. In certain situations, some of this noise can be used very advantageously to mask other noises which by themselves could be annoying.

In summary, we have tried to show that:

- (1) air flow noise is important to industrial hygienists interested in hearing conservation;
- (2) air flow can produce noise in a variety of

ways; and (3) such noise can be reduced to produce an acceptable environment consistent with the activities carried on in that environment.

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FELLOWSHIPS IN INDUSTRIAL HYGIENE

THE ATOMIC Energy Commission is offering special fellowships in industrial hygiene. Training will be received at Harvard University, the University of Cincinnati, or the University of Pittsburgh during the academic year, beginning with the fall term. Fellows must be under 35 years of age; be a citizen of the United States; have a bachelor's degree in physics, chemistry or engineering; and be acceptable for graduate work at the university to which they are assigned. The basic stipend for the academic year is \$2500 with an additional \$350 for a spouse and \$350 for each dependent child. Further assistance is given by payments for tuition, fees, travel, and related graduate work previously completed. No commitment regarding future employment is involved.

Forms and detailed information may be obtained from Industrial Hygiene Fellowship Office, Oak Ridge Institute of Nuclear Studies, Oak Ridge, Tennessee. Completed applications and supporting material must reach the Institute not later than March 1, 1959. Appointments will be made on or about April 1, 1959.

Some Noise Control Methods Used in Industrial Operations*

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THE various methods or techniques for controlling noise are often classified in categories such as noise reduction at the source, noise control of the transmission path, substitution of less noisy processes, and a few others. While it is acknowledged that the most effective means of noise control is reduction at the source, this approach often is not practical where machines or equipment already in use are concerned. Consequently, the ultimate solution to many noise problems must be the responsibility of the machinery manufacturer rather than the user. There are, however, measures which can be taken at the production plant level to control noise exposures. Because of the complexity of most factory noise problems all possible approaches should be considered before any action is taken. This paper describes several examples of noise control attempted in different industries with varying degrees of success.

Control by Enclosure

Controlling the transmission path of air-borne sound seems to have more frequent application in factory noise problems than any other single approach. This can be done in a number of ways by employing different types of attenuating structures and enclosures. The most practical enclosure may depend on a variety of economic and operational considerations.

The most satisfying results are realized when a noisy machine can be totally enclosed near the source to take advantage of the large transmission loss provided by almost any properly designed wall or panel. When doors or access panels are required in a total enclosure, they should be equipped with rubber or similar material sealing all edges or joints and preferably a pressure type latch. Figure 1 shows individual total enclosures that were provided for slotted tumblers used to separate scrap metal from parts. The parts are cup-like objects stamped from either 18 or 20 gauge cold-rolled sheet steel. The material is loaded or shoveled into the

tumblers by hand. As the tumblers rotate, the thin, washer-like pieces of scrap fall through the slots in the tumbler wall into a pan on the floor. When the operation is completed the scrap pan is removed and an empty tray is placed on the floor to catch the parts.

The enclosures consist of quarter-inch tempered masonite over one inch thick fibrous sheathing on the outside of 2 x 4 studs, and another one inch thick sheathing nailed to the inside of the studs. The studs are located about 18 inches on center and the 4-inch space between the two surfaces of sheathing is filled with a rock wool batts. The doors are of the same construction.

Before and after noise level measurements were made with one tumbler operating. The over-all noise level was reduced 23 db from 111 to 88 at a point in the aisle about five feet in front of the tumbler. This was predominately high frequency noise and reductions of 22 to 24 db were obtained in each of the four octave bands between the frequencies of 600 and 10,000 cps. as shown in Figure 2.

The high attenuation obtainable with total enclosures can also be utilized by reversing this approach. That is, when machines are automatic, semi-automatic or can be operated by remote control, it is sometimes more convenient to enclose personnel or machine operators than it is to enclose the noisy machine. This method of control was particularly suitable for paper mill machine rooms when considering that the dimensions of a paper making machine are anywhere from 100 to 200 feet in length and 15 to 30 feet in width.

Figure 3 shows a specially designed booth installed in the aisle between two paper machines to provide a relatively quiet area for some of the machine room employees. By spending as much time as possible in this booth, the duration of the noise exposure is reduced considerably. It is reported that during the average working day, machine operators can spend approximately 50 per cent of the time in this booth.

The walls consist of 16 gauge aluminum sheet

* Presented at the Industrial Health Conference, Atlantic City, New Jersey, April 25, 1958.

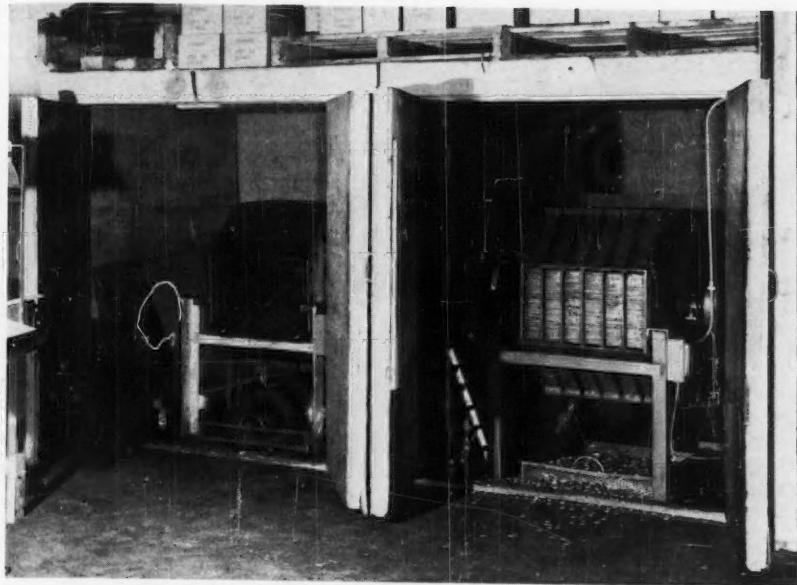


FIGURE 1. Individual total enclosures for slotted tumblers—doors open.

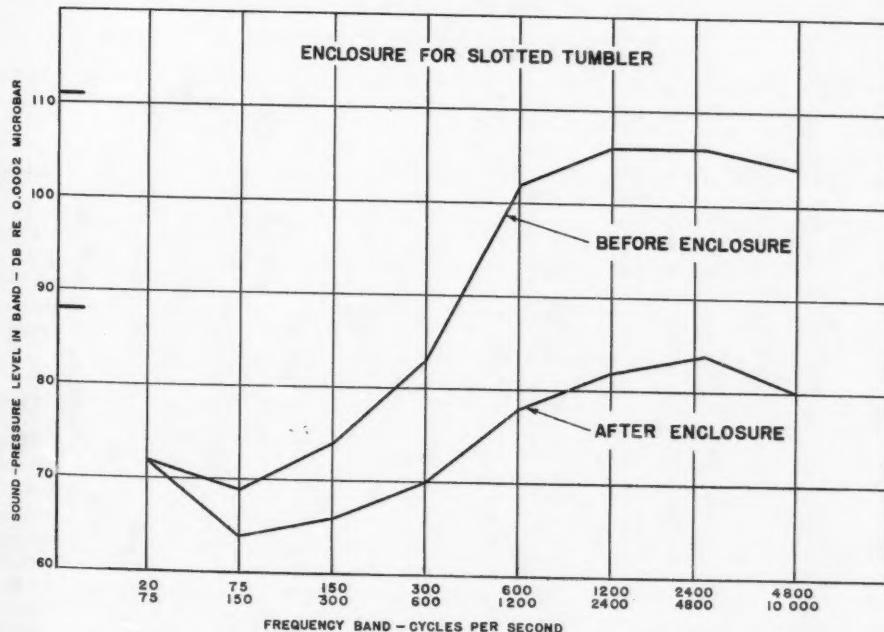


FIGURE 2. Noise levels before and after enclosure of slotted tumblers.

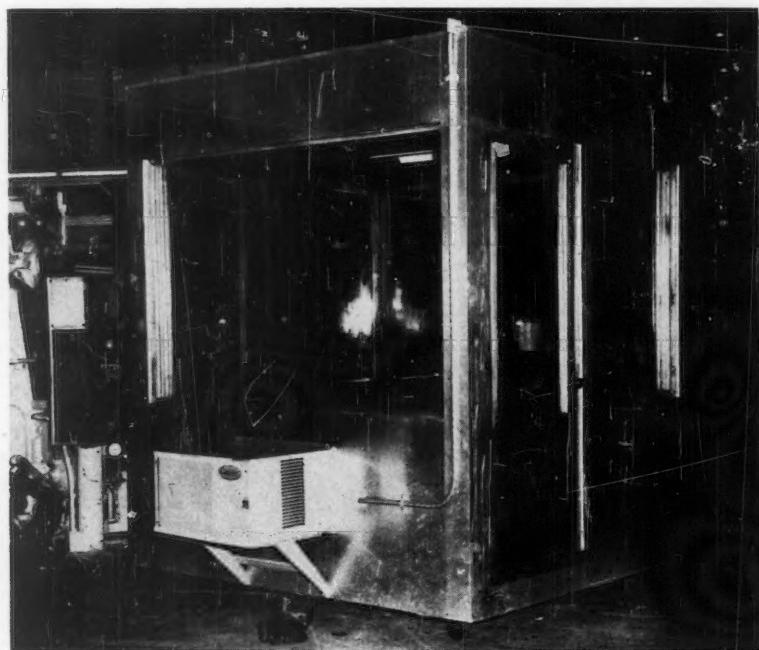


FIGURE 3. Specially designed booth provided for paper machine operators in paper mill.

over $\frac{1}{2}$ -inch plywood on the outside and $\frac{1}{8}$ -inch perforated tempered hard board on the inside. The four-inch space between the wall surfaces contains a two-inch thick blanket insulation fastened to 1×2 and 2×2 furring strips. For the floor, $\frac{1}{8}$ -inch cork tile was laid directly on $\frac{3}{4}$ -inch sheathing grade fir plywood, supported by four-inch steel channels, 22 inches on center. The ceiling is the same construction as the walls except that $\frac{1}{2}$ -inch acoustical tile was substituted for the perforated hardboard.

Since this is in effect an observation booth, it was essential that good visibility be provided in all directions. Except for corner posts and door frames, there are no obstructions to visibility. All windows, including those in the doors, are thermopane with $\frac{1}{4}$ -inch plate glass and $\frac{1}{2}$ -inch air space. The two largest windows in opposite walls are $8\frac{1}{2}$ inches by 50 inches.

The booth has two doors with one opening towards each paper machine. The doors are $1\frac{3}{4}$ inch thick, hollow-core wood doors with a neoprene gasket on all contact surfaces. The booth is constructed on a welded steel frame and mounted on ball-bearing swivel casters so that it can be moved by just rolling it along

the floor. A small air conditioning unit is in one wall and electrical service is provided from overhead by means of a flexible conduit. The booth is approximately seven feet square and eight feet high and has a built-in desk along one wall.

The average over-all noise level in the area just outside the booth is 108 db and the over-all noise level inside is 88 db. Octave band levels were reduced in the range of 20 to 25 db. After a successful trial period in this particular paper mill, the same company provided a similar booth in their other mill.

Another application for the total enclosure is to isolate a noisy operation and the personnel necessary for the job and thereby reduce the number of people exposed to the noise. Two of the noisiest operations in boiler fabrication are the belling and beading of tubes, both of which are performed with pneumatic hammers. These operations were originally performed in a large, open working area exposing many workers to high intensity noise during frequent intervals. To confine this high level noise to the immediate area surrounding the operation, a large enclosure was constructed.

The enclosure consists of an outer wood sur-

face with batts of sound-absorbing material lining the entire inside wall and ceiling surfaces. It was constructed with large hinged double doors at one end providing the necessary access for small rail flatcars.

Noise level readings made before and after enclosure at a work station 37 feet from the beading operation showed noise reductions in the 1,200 to 2,400, 2,400 to 4,800, 4,800 to 10,000 cps frequency bands of 14 db, 17 db, and 16 db, respectively. This enclosure is, no doubt, giving larger noise reductions than those indicated by these values because the final readings with the enclosure were approximately the same as the ambient noise level in the area. This arrangement does not reduce the noise for the operators who must be inside the enclosure so they must wear personal protective devices.

In some cases, plant layout may allow complete isolation by merely adding a single partition. Very high noise intensities were encountered in a small building where superchargers are tested. A 150-horsepower dc electric motor drives the superchargers under test at 3,500 rpm. The room surfaces are brick and concrete. Although workers must be in the immediate vicinity of the rest stand for short periods to make adjustments and record certain data, the majority of their time is spent at a

control panel 12 feet away from the test stand.

A full partition from ceiling to floor and wall to wall was constructed between the test stand and the control panel in an attempt to reduce the noise at the control panel. The over-all noise level at the center of the test stand area which is about 12 feet from the super charger is 127 db. The over-all noise level at the control panel in back of the partition was reduced to 100 db. The observation window is $\frac{1}{2}$ -inch multi-plate bullet-resistant glass. A door in the partition to the left of the observation window provides the necessary access to the test stand area. The workers wear ear protective devices at all times while in that area.

Although total enclosures are more effective, enclosures with openings which range from less than a square foot to many square feet are usually more practical in industry. With such partial enclosures, almost any reasonably impervious panel provides sufficient transmission loss because most of the noise will leak through the openings and this will be the limiting factor. All enclosures should be lined with sound-absorbing material, however.

Figure 4 shows the enclosure of a small foundry shake-out for brass and bronze fittings which was enclosed with fairly good results. Since the shake-out is continuously fed by con-



FIGURE 4. Enclosure for small foundry shakeout.

veyor at one end and unloaded by hand at the opposite end, it was necessary to leave openings for this purpose. The openings were made as small as possible and fitted with curtains of heavy rubberized canvas to reduce the noise transmitted through them.

The enclosure consists of quarter-inch masonites over half-inch fibrous panel. The sides, ends and top of the enclosure were fabricated as separate panels on metal frames and can be partially or totally disassembled for maintenance purposes. The panels are held together with hinges welded to the metal frame and can be removed by knocking out the hinge pins. The enclosure sits on strips of soft fibreboard which provides a reasonably good seal with the floor.

The parts are automatically dumped from pans on an overhead conveyor into a chute at the rear of the shake-out. The chute carries them through the rear opening to the shake-out table. The greatest noise reduction was found to be at an inspection table about 6 feet directly to the side of the enclosure. At that location, the over-all noise level was reduced from 101 to 94 db. The critical frequency band levels in the 600 to 1200 and 1200 to 2400 cps bands were both reduced 10 db from 96 to 86 db.

A one-sided enclosure or barrier is generally

less effective than any of those previously described. However, in situations where a more complete enclosure would be prohibited due to accessibility and material flow requirements, even a single barrier can produce worth-while results. A partial enclosure is useful in producing a shadow effect in one direction determined mainly by the relative position of the barrier and the noisy machine. This shadow effect applies to the direct field from a noise source and is limited to the higher frequencies to the extent that the dimensions of the barrier must be several times the wave length.

The barrier shown in Figure 5 was provided to reduce the high level direct field noise from the radial saw in the area directly behind the saw. It consists of six wood-frame panels, each of which is approximately 8½ feet high, 4 feet wide and 3¾ inches thick. The back surface is $\frac{3}{16}$ -inch masonite and the panels are packed with fibre glass batts which are compressed slightly and held in place with quarter-inch square mesh galvanized chicken wire. The two end or wing panels can be rotated approximately 90 degrees. A $\frac{3}{16}$ -inch thick rubber hinge extends the full length of the wing and adjacent panels. This permits the rotating motion and also seals the cracks.

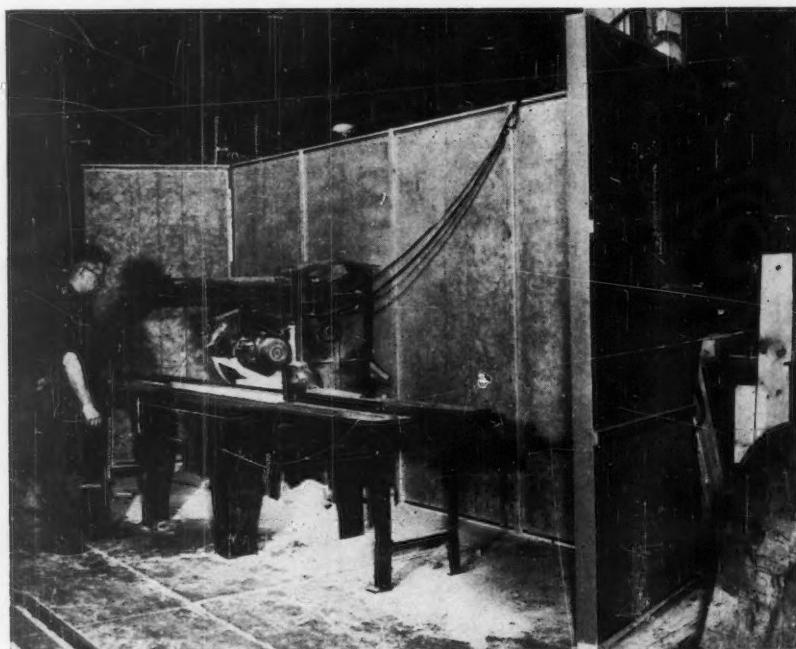


FIGURE 5. Barrier used as partial enclosure to control noise produced by a radial saw.

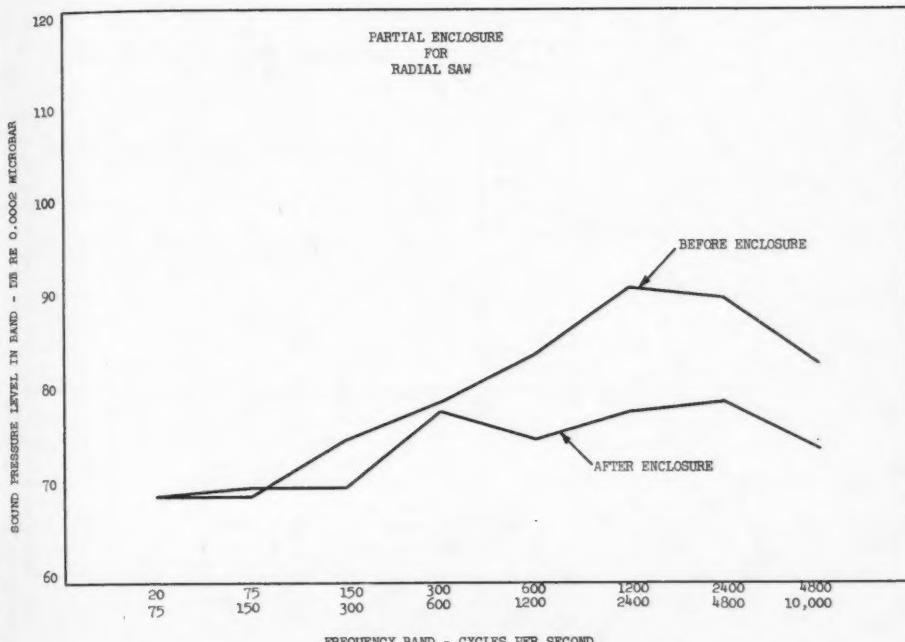


FIGURE 6. Noise levels at a point ten feet in back of a radial saw before and after partial enclosure.

The noise level measurements shown in Figure 6 were made at a work bench about 10 feet behind the saw while cutting 1- by 12-inch soft lumber. Octave band levels in the higher frequencies were reduced in the order of 10 db.

Control by Snubbers and Mufflers

Attenuating devices are commonly employed in reducing exhaust noises from fans, pumps, blowers, internal combustion engines and air-operated equipment. For example, the vacuum pumps for the suction presses on a paper making machine originally discharged directly through a short pipe into an open sewer under a metal grating in the floor. This arrangement produced an over-all noise level of 120 db at a point three feet directly above the sewer opening. The vacuum pump is rated at 18 inches of mercury when operating at 360 rpm and the discharge is a mixture of air and water. A commercial separator snubber which separates the water and air was installed in the discharge line from the pump. The separator snubber has the water outlet at the bottom extending down into the sewer and the air outlet at the top. This single unit reduced the over-all noise level from 120 to 112 db.

Because a greater reduction was desired, an additional snubber was connected to the air outlet of the separator snubber and this reduced the over-all noise level from 112 to 102 db. The results of the octave band analysis are shown in Figure 7.

In the same paper mill, a separator and a snubber were also connected to the discharge pipes of two other vacuum pumps rated at 17.5 inches of mercury when operating at 680 rpm. The over-all noise level at this location was reduced from 116 to 101 db.

One of the simplest and least expensive noise control measures is the muffling of exhaust air noise from certain air operated equipment. For example, a small, table-mounted, air-operated machine which performs a degating or trimming operation on molded plastic pen parts originally discharged exhaust air directly into the atmosphere at the rear of the machine producing a maximum over-all reading of 114 db on the sound level meter. The noise produced by the air exhaust was intermittent and of short duration but occurred every few minutes.

A small commercial muffler was installed on the exhaust air outlet which reduced the over-all noise level to 88 db. The high frequency

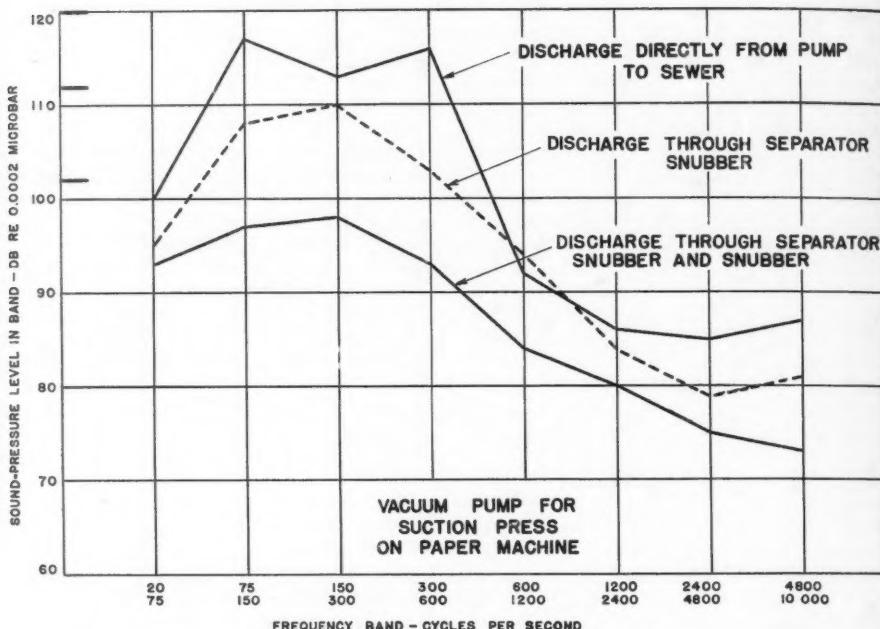


FIGURE 7. Octave band analysis showing effect of snubbers on vacuum pump noise.

noise was reduced to a level where it is hardly noticeable above the ambient noise in the room.

This particular plant has many air operated machines operating at air pressures of 40 to 110 psi. At present they have approximately 150 mufflers installed on machines throughout the plant with individual machines having anywhere from one to six mufflers.

Control by Substitution

Gears are frequently associated with the production of noise and much of the noise produced by a custom-built, paper-tag-converting machine was contributed by a heavy cast gear train. The machine performs a punching and cutting operation as a narrow strip of paper is fed through the point of operation. The entire drive assembly was replaced with a commercially available fluid drive transmission and a custom-built oil immersed roller chain drive.

Noise level readings taken at the machine operator's position showed that the over-all noise level was reduced from 95 to 83 db. The noise measurements were made while the plant was shut down so that the background noise was well below the machine noise. The transmission noise is now less than the noise

produced by the remainder of the machine mechanism.

The first step in an experimental project undertaken to reduce gear noise on textile machinery involved the substitution of a nonmetallic spur gear for one of two mating gears on a wool yarn twister machine. The gears in question have relatively low load requirements but operate at fairly high speeds. The gear diameters are approximately 2½ inches and 5 inches and the nonmetallic gear was substituted for the smaller of the two. On the first trial, the nonmetallic gear showed excessive wear after two months of operation and had to be removed. Because the gear was worn unevenly, the alignment was checked and found to be faulty. The shaft was straightened, new bearings were installed and the same type of nonmetallic gear has now been in use approximately 18 months with no noticeable signs of wear.

Noise measurements were made for comparative purposes only with the twister machine operating normally. Other machines in the area were shut off to lower the background noise which was at the same level for both tests. To reduce the effect of noise produced by other sources on the twister, the microphone was placed 18 inches from the mating gears and in

line with the shaft. Noise reduction in the octave bands between the frequencies of 150 cps and 4800 cps varied from 3 to 7 db.

The possibility of developing new and quieter tools and equipment or substituting a quieter method of doing a particular operation offers many opportunities for noise reduction. In a plant which manufactures air conditioning equipment, pneumatic hammers were formerly used to bend and close seams on sheet metal fan housings. This operation produced an over-all noise level in the immediate area of 106 db and the 600 to 1200 cps frequency band was the highest level at 103 db. Attempts to dampen the vibrations of the large radiating surface provided by the housing resulted in some noise reduction but were considered unsatisfactory. Pinch roller machines which are commercially available were first provided to perform this operation on the

smaller fan housings of about 12 inches in diameter. When it was decided to use similar machines to perform this operation on housings of all sizes, the machines were not available to handle the larger housings. A pinch roller machine which can handle all of the large housings was built by the user; in addition to completely eliminating the high level noise, it has also greatly reduced the time required for the job.

These examples are not intended to be the ultimate solutions to the particular noise problem involved. Rather, they are control measures which have actually been applied with reasonably satisfactory results. The main purpose behind these illustrations is not only to suggest similar solutions to similar problems but to stimulate thinking and experimentation which will lead to the development of new and better noise control measures.



HYGIENIC GUIDE SERIES

Ethylene Oxide

(Epoxyethane, Oxirane, Dimethylene Oxide)

I. Hygienic Standards

A. RECOMMENDED MAXIMUM ATMOSPHERIC CONCENTRATION (8 hours): 50 parts of vapor per million parts of air, by volume (ppm).²

(1) Basis for recommendation: Toxicological observations on animals.^{4, 5}

B. SEVERITY OF HAZARDS:

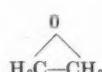
(1) Health: Moderate, for both acute and chronic exposures. Volatility is high and pulmonary absorption is rapid. Animal studies have shown irritation of the eyes and respiratory tract. High concentrations cause vomiting, convulsions, and death, with the lungs, liver, kidneys, and adrenals showing evidence of injury. Repeated exposures to about 100 ppm appear to be safe, but depression of animal growth and delayed impairment of nervous system functions occur above 200 ppm. Contaminated rubber⁶ and aqueous solutions contacting the skin can cause primary skin injury. Sensitization may occur.⁶

(2) Fire: High. Explosive limits are 3-100% by volume.² Flash point is below 0° F.

C. SHORT EXPOSURE TOLERANCE: The estimated LC₅₀ for four hours' exposure is approximately 800 to 1500 ppm, depending upon the species.⁵

II. Significant Properties^{2, 7}

Chemical formula:



Molecular weight:

44.1

Specific gravity:

0.8711 (apparent)

Boiling point:

20°/20°C

10.7°C

Vapor pressure at 20°C: 1095 mm Hg

Relative vapor density: 1.5

Solubility: Completely in water, alcohol, ether.

At 25°C and 760 mm Hg,

1 ppm of vapor: 0.0018 mg/liter
1 mg/liter 556 ppm

III. Industrial Hygiene Practice

A. RECOGNITION: May be recognized by its sweet odor and irritant effects. The odor is inadequate to serve as a warning of dangerous concentrations. Ethylene oxide is used primarily as an intermediate in the manufacture of ethylene glycol, polyglycols, glycol ethers, ethanolamines, plastics, and surface active agents. It has direct use as a sterilizing and fumigating agent.

B. EVALUATION OF EXPOSURES:

(1) Direct instrumentation: An instrument using impregnated silica gel, and capable of detecting 10 ppm, has been described.⁸

(2) Chemical: Collection in an all-glass scrubber, containing a 0.100N solution of sulfuric acid saturated with magnesium bromide, followed by titration of the excess acid with standard sodium hydroxide.⁹

C. RECOMMENDED CONTROL PROCEDURES: Enclosure of processes, accompanied by local or general ventilation. Eye protective devices should be worn at all times. Personnel should be instructed in the safe handling of this compound.

IV. Specific Procedures

A. FIRST AID: Clothing and shoes contaminated with ethylene oxide should be

- removed and the skin thoroughly washed. In case of eye contact, irrigate immediately with large quantities of water for at least 15 minutes.
- B. SPECIFIC MEDICAL PROCEDURES: No specific preplacement requirements. Treatment of exposure is non-specific.

V. Literature References

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Arsenic and Compounds (Except Arsine)

I. Hygienic Standards

- A. RECOMMENDED MAXIMUM ATMOSPHERIC CONCENTRATION (8 hours): 0.5 milligram of arsenic per cubic meter of air (mg/m^3).²
- (1) Basis for recommendation: Human experience.
- B. SEVERITY OF HAZARDS:
- (1) Health:^{3, 9} High. Acute systemic poisoning is rarely of occupational origin. Skin lesions, and perforation of the nasal septum are the commonest results of inadequate protective measures for workers exposed to arsenious oxide, arsenites, and arsenates. Carcinogenic effects involving both skin and respiratory passages have been reported,⁶ but this has not been confirmed by United States experience.¹¹ Gastro-intestinal disturbances and polyneuritis have been found in chronic poisoning.⁷ Arsenic trichloride and certain of its derivatives (chlorvinyl dichloroarsine, etc.) are vesicants, in addition to being highly irritating to the respiratory tract.
- C. SHORT EXPOSURE TOLERANCE: Not known. The lethal dose for humans of soluble arsenic compounds, taken orally, is probably between 0.1 and 0.3 gm.⁸
- D. ATMOSPHERIC CONCENTRATION IMMEDIATELY HAZARDOUS TO LIFE: Not known

for most compounds. For arsenic trichloride, 2.5 mg/liter of air produced death in mice after 10 minutes' exposure,⁴ and 0.2 mg/liter of air killed cats in four days after 20 minutes exposure.⁵

II. Significant Properties

Chemical symbol:	As
Atomic weight:	74.9
Specific gravity (black crystalline form):	5.7
Sublimation temperature:	15° C (approx.)
Solubility:	In nitric acid

III. Industrial Hygiene Practice

- A. RECOGNITION: Major use as compounds for economic poisons.
- B. EVALUATION OF EXPOSURES:
- (1) Direct instrumentation: None.
- (2) Chemical method: Collect dust or fumes with electric precipitator, filter paper, or impinger. After conversion to arsine with reducing agents, determination may be made by Gutzeit test or with silver diethyldithiocarbamate reagent.² For urine determinations, the molybdenum blue method for arsine has been used.¹⁰
- C. RECOMMENDED CONTROL PROCEDURES: Keep atmospheric concentration below

acceptable limits by enclosure or ventilation. Protect skin from direct contact with soluble arsenic compounds, and especially from the vesicant liquids such as the trichloride, Lewisite, etc.

V. Specific Procedures

- A. FIRST AID: Remove from exposure and call physician.
- B. SPECIAL MEDICAL PROCEDURES: Urinary excretion of arsenic is a useful index of exposure, but dietary factors may also increase urinary levels.¹⁰ The influence of these should be ruled out before significance is attached to any increase. Treatment with BAL should be considered in suspected cases of arsenic intoxication.

V. Literature References

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Because of space limitations, it is impossible to list all methods of exposure evaluation. The selections have been made on the basis of current usage, reliability, and applicability to the usual industrial type of exposure. Any specific evaluation and/or control problem will involve professional judgment. This can best be done by professional industrial hygiene personnel.

Respiratory protective devices are commercially available. Their use, however, should be confined to emergency or intermittent exposures and not relied upon as primary means of hazard control.

A relative scale is used for rating the severity of hazards: nil, low, moderate, high, and extra hazardous.

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News of Local Sections

Chicago

The first meeting of the 1958-1959 year was held September 3rd. Since it is the custom for the immediate Past-President to be the speaker at one of our meetings, this assignment was very effectively handled at our first meeting by Mr. Fred Cook of Bituminous Casualty Corporation. Fred spoke on "An Insurance Company's Approach to Industrial Hygiene."

"What and how well we see depends upon our selection and application of light sources, how they operate and their effect on color." This statement, by means of a demonstration assembly of lighting equipment, was proved at our meeting on October 10th, by Mr. R. M. Smart, engineer, Sylvania Electric Products, Inc. Mr. Smart's interesting presentation was entitled "Facts of Light."

For some meetings the program committee occasionally has difficulty in obtaining a speaker, but for our meeting November 6th, we were fortunate and had two. First, Ken Nelson, President of A.I.H.A., brought us up to date on the affairs of our national association. Then Robert A. Kehoe, M.D., addressed us on the subject—"Research and Professional Practice in Industrial Hygiene." The talk by Dr. Kehoe, given in his usual fine manner, renews our faith in the work we are doing and makes us aware of our responsibilities in the field of industrial health.

Mr. Nelson and Dr. Kehoe were in Chicago to participate in the Lead Hygiene Conference of the Lead Industries Association at the Drake Hotel on November 6th and 7th. Many Chicago Section members attended this excellent conference as guests of L.I.A.

New Jersey

At our meeting October 6th, Cyril M. Harris, Ph.D., Associate Professor of Electrical Engineering, Columbia University, discussed "Noise Control in Industry." As most of you know, Dr. Harris is the author of *Handbook of Noise Control*. Thirty-three members attended this very interesting and informative meeting.

Pacific Northwest

Officers for 1958-1959 are: President—Walter H. Poppe, Jr., Boeing Airplane Company, Seat-

tle; President-Elect—Daniel J. Bessmer, Puget Sound Naval Shipyards, Bremerton, Washington; Secretary-Treasurer—William C. Applegate, Occupational Health Section, Oregon State Board of Health, Portland; Director—Frank Adley, General Electric Company, Richland, Washington.

The Third Annual Meeting of the Pacific Northwest Section was held September 13th, at the Boeing Airplane Company, Renton, Washington. This was an all day and evening session with twelve papers presented, a tour of the plant, and a banquet. At the banquet, Dr. Ralph R. Sullivan, Director of the Occupational Health Section, Oregon State Board of Health, was presented the J. M. Dalla Valle Award. The newly created award, presented for the first time this year, was given to Dr. Sullivan for his significant contribution to industrial health in the Pacific Northwest.

Philadelphia

Fifty-four persons, almost evenly divided between the IMA and AIHA attended our joint meeting at the Penn-Sherwood Hotel on May 27th. Dr. Sidney Cobb of the University of Pittsburgh presented an interesting talk on the application of epidemiology to industrial hygiene and health problems.

At our meeting at the Engineer's Club on November 11th, we plan to have a panel discussion of recent advances in the field of radiological health and safety. The Philadelphia Section will be host this year for the Tri-Section Meeting in December.

Obituary

William R. Phillips, 56, died at Atlanta, Georgia on July 11, 1958. He was widely known for his work in safety. At the time of his death he was District Safety Director for Lumbermens Mutual Casualty Company and had been with the company since 1940. He graduated in mechanical engineering from Georgia Institute of Technology in 1923. He was a Registered Professional Engineer and a member of the American Society of Safety Engineers. He had been a member of A.I.H.A. since 1953.

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